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Electrochemistry
Glass

BEHAVIOR OF A GLASS ELECTRODE IN NON-AQUEOUS MEDIA

IV. ERRORS OF THE GLASS ELECTRODE IN ACID AND ALKALINE REGIONS IN ETHANOL AND IN MIXTURES OF ETHANOL AND WATER

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As is known, the potential of a glass electrode varies linearly with the pH of a solution over a wide area. A deviation from rectilinearity is observed in strongly alkaline and acid regions. In the alkaline region, the glass electrode potential - solution pH curve, or what is the same, the calibration curve of the glass electrode at a certain pH value, deviates from rectilinearity and often passes through a maximum.

As was established by Nikolsky, the deviation from rectilinearity of the potential - solution pH curve in an alkaline region is explained by a shifting of the hydrogen function of the glass electrode to a sodium function; the length of the rectilinear portion of the glass electrode calibration curve being related, according to Nikolsky, [1] to the exchange constant K of the glass ions, where:

$$K = \frac{a_{\text{H}^+} \text{ of the solution } a_{\text{Na}^+} \text{ of the glass}}{a_{\text{H}^+} \text{ of the glass } a_{\text{Na}^+} \text{ of the solution}}$$

a_{H^+} and a_{Na^+} are the activities of the sodium and hydrogen ions in the glass and in the solution.

The location of the break in the Nikolsky calibration curve is also related to the value of the exchange constant for the glass ions. The formula for the glass electrode potential - glass constant curve has the following appearance:

$$E = E_0 + \frac{2.3RT}{F} \log (a_{\text{H}^+} \text{ solution} + K a_{\text{Na}^+} \text{ solution})$$

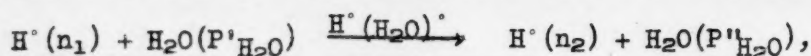
where E and E_0 are the potential and null potential of the glass electrode.

From the literature data, a deviation from rectilinearity of the potential - solution pH curve is also observed in the acid region, but with a reverse sign to that of the alkaline region.

Having investigated the behavior of the glass electrode over a wide pH interval we observed for the first time not only a deviation from rectilinearity in a strongly acid region, but also the fact that the characteristic curve for the glass electrode passes through a minimum.

Examining the glass electrode as a membrane through which the hydrated hydrogen ions pass, Dole [2] explains the deviation in the acid region by the difference in activity of water on both sides of the membrane. Dole also expands his theory to non-aqueous solutions, maintaining that the ordinary glass electrodes cannot be used for measuring the activity of hydrogen ions in non-aqueous solutions. According

to Dole, the electrode reaction at the glass electrode can be written as follows:



where $H^+(H_2O)^*$ is the hydrated proton. Then the equation for the glass electrode potential will take the form:

$$E = \frac{2.3RT}{F} \log \frac{a_1}{a_2} + \frac{2.3RT}{F} \log \frac{P'(H_2O)}{P''(H_2O)},$$

where P is the vapor tension of water.

Calculating the equation for the hydrogen electrode from the equation for the glass electrode, Dole found the magnitude of error of the glass electrode equal to:

$$\Delta E = \frac{2.3RT}{F} \log a_{H_2O},$$

where $a_{H_2O} = \frac{P'(H_2O)}{P''(H_2O)}$ - the activity of water in the external solution.

And consequently for an anhydrous medium, in particular for anhydrous ethyl alcohol where the activity of water becomes negligible, but where an aqueous solution is contained inside the electrode, the error reaches such a magnitude that the glass electrode cannot be used for measurement.

Dole then draws the conclusion that the glass suitable for work in non-aqueous solutions should allow only unhydrated hydrogen ions to pass through.

As a result of experimental investigations in 1938 Izmailov and Belgova [3] found that in alcoholic mixtures containing 50 and 70% ethyl alcohol and at a pH interval of 4 to 8, the glass electrode behaves exactly as in aqueous solution.

Later, Izmailov and Frantsevich-Zabludovskaya [4], investigating the behavior of glass electrodes, made from electrode glass of the usual composition, in mixtures of ethyl alcohol and water, in acetone mixtures and in 90% methyl alcohol, showed that the glass electrode was fully suitable for the measurement of pH in non-aqueous solutions.

We continued the investigation of the behavior of the glass electrode in water and in mixtures of ethyl alcohol and water, up to absolute ethyl alcohol. In each case the glass constant was calculated, and this done, a relationship was found between the constant measured and the molarity of the alcohol in the mixture. We also calibrated the glass electrode with buffered solutions in absolute methyl alcohol.

EXPERIMENTAL

Alkaline Region

In our work we conducted an investigation of the behavior of glass electrodes in the media shown in Table 1.

We used these alcohol-water mixtures since their HCl activity coefficients were known.

We investigated glass of three different compositions. The compositions of the glass are given in Table 2.

Spherical electrodes were prepared from the glass, according to Haber. In all cases the inside of the electrodes was filled with an aqueous Weibel solution. The prepared electrodes were submerged in 0.1 N HCl for 3 - 5 days. Thereafter the electrodes were stored in distilled water.

TABLE 1

Expt. No.	Solvent (% by weight)	Molar fraction of the solution	pH intervals
1	Water	-	- 0.9 + 14.0
2	20 ethanol.....	0.0891	- 0.8 + 14.3
3	71.9 ethanol.....	0.5	- 0.6 + 14.86
4	88.5 ethanol	0.75	- 0.5 + 15.56
5	93.5 ethanol	0.85	- 0.5 + 15.85
6	100.0 ethanol	1.0	+ 0.6 + 14.1
7	100.0 methanol	1.0	+ 0.9 + 15.8

TABLE 2

Expt. No.	Type of glass	Composition of the glass (in %)				
		SiO ₂	Na ₂ O	CaO	R ₂ O ₃	Remainder
1	Yuz glass.....	72.0	20.0	8.0	-	-
2	McInnes and Dole Glass (Corning 015).....	72.0	22.0	6.0	-	-
3	"Eldaf" 4 glass	66.93	22.84	4.92	0.55	4.76

Measurements with the glass electrodes were carried out with a vacuum-tube amplifier in conjunction with a Raps potentiometer, the construction of which is described in detail by Izmailov and Zabara [5].

The composition of the cell, during measurement of aqueous solutions and mixtures of alcohol and water by means of the glass electrode, was the following:

Hg	Hg ₂ Cl ₂ KCl sat.	KCl sat.	Investigated solution	Glass	Weibel's aqueous solution	Weibel's Hg ₂ Cl ₂ solution	Hg
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In the case of absolute methyl and ethyl alcohols, the aqueous calomel electrode and the aqueous bridge was eliminated from the cell. All the measurements were conducted in a circuit with a quinhydrone electrode placed in an alcoholic solution which served as a standard half-cell and consisted of 0.01 N HCl and 0.009 N NaBr.

Contact was accomplished by means of a bridge filled with a saturated solution of KBr in absolute alcohol.

For calibrating the glass electrodes in water, a series of buffer solutions was prepared: according to McElvain, pH 2.7-8.0; according to Sorensen, pH 9.3-10.1; and according to Ringer, pH 11.3-12.3. For higher pH values solutions of sodium hydroxide were used.

In a strongly acid region (pH from -1 to +2) the electrodes were calibrated with hydrochloric acid solutions.

A series of buffer solutions, mixtures of an acid and its salt, were prepared in ethanol-water mixtures and in absolute ethyl and methyl alcohols (Li salt was used for absolute ethyl alcohol and sodium salt for all the other cases).

The composition of the buffer solutions are shown in Table 3. For the more alkaline regions, solutions of sodium hydroxide were prepared in mixtures of ethyl alcohol and water and in solutions of sodium alcoholate in absolute alcohols, having the pH values shown in Table 3.

TABLE 3

Expt. No.	Buffer	Concentration		Ethyl alcohol (% by weight)					Methyl alcohol - 100%
		acid	salt	20.0	71.9	88.5	93.5	100.0	
				pH of the buffer solutions					
1	Trichloroacetate	0.1	0.1	-	-	-	-	4.0	4.0
2	Salicylate.....	0.1	0.01	3.4	3.8	4.56	5.0	5.9	6.0
3	Salicylate.....	0.01	0.1	5.1	5.6	6.24	6.8	8.1	-
4	Benzoate.....	0.1	0.1	5.7	6.3	6.9	7.4	-	8.4
		0.01	0.1	6.6	7.3	8.0	8.4	-	-
	Veronate.....	0.1	0.01	8.2	8.7	9.3	9.8	11.5	10.1
5		0.001	0.1	9.6	10.1	10.7	11.3	12.7	12.4
6	Phenolate.....	0.1	0.01	10.0	10.9	11.5	12.0	13.4	12.2
		0.1	0.1	11.3	12.0	12.6	12.9	14.1	13.4
				pH of the alkaline solutions					
7	Solutions of sodium hydroxide or sodium alcoholate.....	-	-	14.3	14.86	15.56	15.85	-	14.0 14.4 15.8

The pH of all the solutions was measured with a hydrogen electrode in a concentration cell relative to the standard, a 0.1 N HCl in the corresponding solvent; i.e., the standard was an infinitely diluted solution of ions in the given medium and not in water.

The pH values were calculated from the data on the activity coefficients of 0.1 N HCl [5]. In the case of the alcohol-water mixtures the calculation was made according to the formula:

$$\log a = \frac{E_0 - E}{0.1154} \text{ at } 18^\circ$$

and consequently, $\text{pH} = \frac{E_0 - E}{0.1154}$. The values for the E and E_0 used in our cells were taken from the work of Harned [6].

The glass electrodes were first calibrated by aqueous buffer solutions. The results of the calibration were plotted graphically, as the potential - solution pH curve. The calibration curves for Yuz glass and MacInnes and Dole glass in aqueous buffer solutions are given in Figs. 1 and 2. The calibration curve for "Eldaf" glass has an identical appearance. As is evident from the diagrams, the break in the curve for all three glasses lies at $\text{pH} = 113.1$.

Nikolsky and Tolmacheva [7] proposed to calculate the exchange constant of the glass ions by the position of the maximum on the calibration curve of the glass electrode. The equation they proposed is of the form:

$$-\log K = 2\text{pH}_{\max} - \text{pK}_1,$$

where pH_{\max} is the pH value at the break point of the calibration curve, and pK_1 is the ion product of the medium.

Having substituted the pH_{\max} values of the calibration curves in the equation, we found that the value for the exchange constant of the glass ions for all three glasses in water was $K = 6.31 \cdot 10^{-13}$.

The glass electrodes were then calibrated in the above-mentioned alcohol-water solutions. The results of the calibration were plotted using the same coordinates. In order to obtain a more coherent picture of the influence of the alcohol content in the solution on the calibration curve of the glass electrode, the calibration

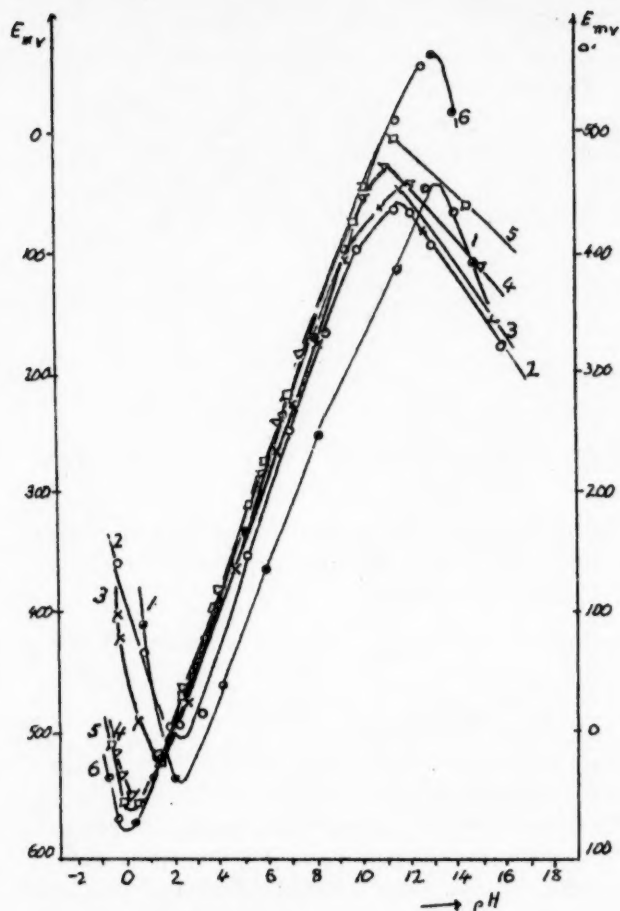


Fig. 1. Calibration curves for a glass electrode made from Yuz glass in ethanol-water mixtures and in absolute alcohol.

Ethyl alcohol: 1 - 100%; 2 - 93.5%;
3 - 88.5%; 4 - 71.9%; 5 - 20.0%.
6 - Water.

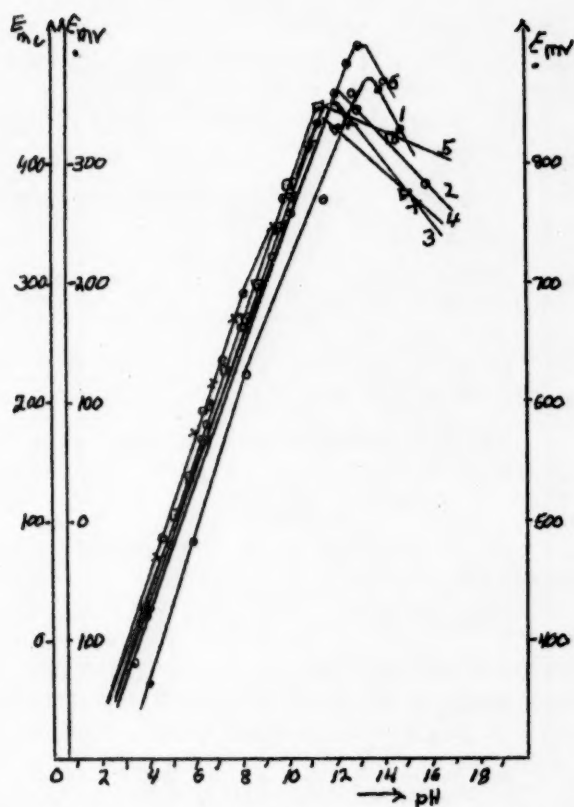


Fig. 2. Calibration curves for a glass electrode made from MacInnes and Dole glass in ethanol-water mixtures and in absolute ethyl alcohol.

Ethyl alcohol: 1 - 100.0%;
2 - 93.5%; 3 - 88.5%; 4 -
71.9%; 5 - 20.0%. 6 - water.

results of the entire series of solutions were plotted on the same graph, but one graph for each glass, on Fig. 1 - for the electrode made from Yuz glass and on Fig. 2 - for the electrode made from MacInnes and Dole glass.

As is evident from the results of the measurements, an increase in the percent of alcohol in the alcohol-water mixtures shifts the position of the break in the calibration curve towards the direction of the higher pH values. Thus, for example, if for 20% ethyl alcohol the break on the calibration curve of the glass electrode made from Yuz glass lies at $\text{pH}_{\text{max}} = 11.0$, then for 93.5% ethanol, $\text{pH}_{\text{max}} = 11.65$. The same situation is observed for MacInnes and Dole glass, but the displacement is somewhat greater.

It should also be pointed out that the deviation from the rectilinear relationship between the potential of the glass electrode and the pH of the solution occurs much sooner for those calibration curves corresponding to a higher alcohol content. Consequently, an increase in the content of alcohol in the solution leads to a

decrease in the rectilinear portion of the calibration curve, which results in a restriction of the range in which the glass electrode may be used for the measurement of pH in ethanol-water mixtures and in absolute alcohol.

Having constructed the calibration curves of the glass electrode in the alcohols, and having consequently obtained the value for pH_{max} , we calculated the values for the exchange constants of the glass ions in the corresponding mixtures of water and ethyl alcohol, using the Nikolsky and Tolmacheva formula. We obtained the values for the ion product of the medium, necessary for calculation of K, from a graph constructed from Kilpi's data [8]. The values for pK_1 were then found to be the following:

	pK_1
100.0% (by weight) ethyl alcohol ...	20.2
93.5% ...	17.35
88.5% ...	16.8
71.9% ...	15.74
20.0%	14.25

The results of our calculations for the exchange constants of the glass ions are given in Table 4.

If, in accordance with this data, the value of pK_1 for absolute ethyl alcohol is taken to be equal to 19.4, then the constant of Yuz glass in absolute ethanol will be equal to $1.26 \cdot 10^{-7}$, and MacInnes and Dole glass equal to $0.3 \cdot 10^{-7}$.

As is evident from the above table, the value for pH_{max} shifts to the more alkaline region with increase in ethyl alcohol content. The value of the glass constant sharply increases on addition of a small quantity of alcohol to the water. Thus, if K of the glass is equal to $6.3 \cdot 10^{-13}$ in water, then in an alcohol-water mixture containing 0.089 molar parts of ethyl alcohol, the K for Yuz glass is equal to $1.78 \cdot 10^{-8}$ and K for MacInnes and Dole glass is equal to $8.9 \cdot 10^{-9}$. By such a tiny addition of ethyl alcohol to the water, the glass constants increase 4-5 exponential units. On changing from the ethanol-alcohol mixture containing 0.089 mol. parts of alcohol to a mixture containing 0.5 mol. parts of ethyl alcohol, the constant increases approximately ten times. But in alcohol-water mixtures with higher and contiguous contents of ethanol, the constant practically does not change either for Yuz glass or for MacInnes and Dole glass.

If the value of the glass constant is compared in water and in absolute ethanol it may be seen that the constant in absolute ethyl alcohol, for both glasses, is greater than the glass constant in water by 6 exponential units.

We also calibrated the glass electrodes made from these glasses in absolute methyl alcohol. A graphical representation of the calibration is shown on Fig. 3. In this case the value of pH_{max} for Yuz glass is equal to 13.3 and for MacInnes and Dole glass it is equal to 13.8. Taking the ion product of absolute methyl alcohol equal to 17.05, we find the value for K for both glasses from the Nikolsky and Tolmacheva formula: for Yuz glass: $K = 2.82 \cdot 10^{-10}$ and for MacInnes and Dole

TABLE 4

Expt. No.	Percent Ethanol (by weight)	Yuz glass		MacInnes and Dole glass		"Eldaf" glass	
		pH_{max}	K	pH_{max}	K	pH_{max}	K
1	100.0.....	13.1	$8.10 \cdot 10^{-7}$	18.45	$2.0 \cdot 10^{-7}$	-	-
2	93.5	11.6	$1.12 \cdot 10^{-8}$	12.10	$1.41 \cdot 10^{-7}$	12.0	$2.24 \cdot 10^{-7}$
3	88.5	11.4	$7.9 \cdot 10^{-7}$	11.80	$1.58 \cdot 10^{-7}$	11.5	$6.31 \cdot 10^{-7}$
4	71.9	11.1	$2.75 \cdot 10^{-7}$	11.45	$6.91 \cdot 10^{-8}$	-	-
5	20.0	11.0	$1.78 \cdot 10^{-8}$	11.15	$8.91 \cdot 10^{-9}$	-	-
6	0.0 (water) ..	13.1	$6.31 \cdot 10^{-13}$	13.10	$6.31 \cdot 10^{-13}$	13.1	$6.31 \cdot 10^{-13}$

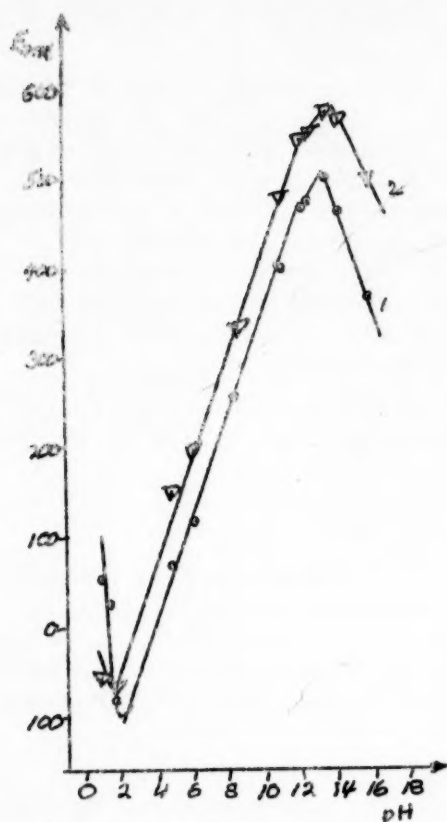


Fig. 3. Calibration curves of glass electrodes in absolute methyl alcohol.
1 - Yuz glass; 2- MacInnes and Dole glass.

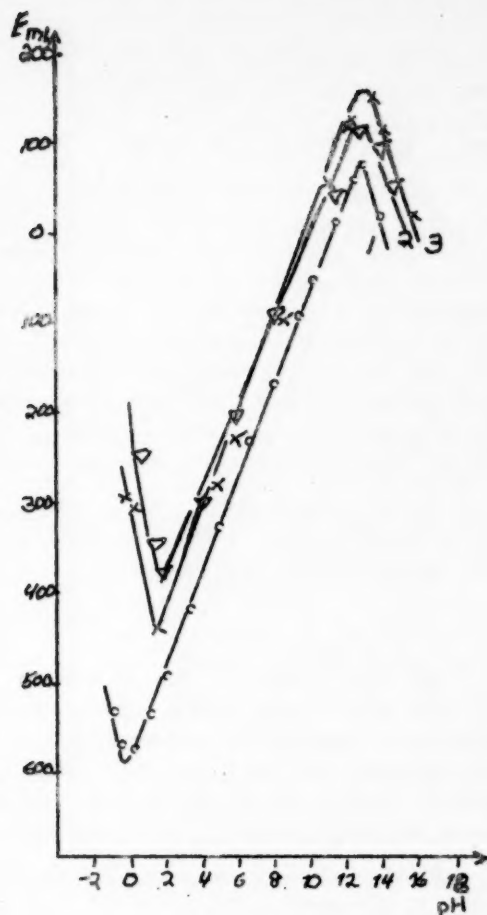


Fig. 4. Calibration curves of a glass electrode made from Yuz glass in absolute alcohols and in water.
1 - in water; 2 - in absolute ethyl alcohol; 3- in absolute methyl alcohol.

glass $2.82 \cdot 10^{-11}$. Izmailov and Frantsevich-Zabludovskaya [8] present data in 90% (by weight) of methyl alcohol for Yuz glass. They found the pH_{max} equal to 13.2 and the value of K equal to $3.98 \cdot 10^{-12}$ at $pK_1 = 15$; i.e., the value for the glass constant in absolute methyl alcohol is greater than in methanol-water mixtures. On the basis of the foregoing it may be concluded that the exchange constant of glass ions increases on changing from water to alcohol-water mixtures and further increases on changing to absolute alcohols.

We were also interested in the question of the relationship of the magnitude of the potential for the same glass electrode in different media at equal pH values. In the work of Izmailov and Frantsevich-Zabludovskaya [4], data are cited for measurement with the same glass electrode in aqueous solutions, in 95% ethyl alcohol and in 90% methyl alcohol. According to their data, the fluctuations observed in the potential of the glass electrode result only from changes in external conditions.

We conducted measurements of aqueous solutions and buffer mixtures in absolute ethyl and methyl alcohols with the same electrode. Since a saturated calomel electrode was substituted by a quinhydrone in the absolute alcohols for the experiments where the absolute alcohols were used in a variable cell with a glass electrode,

it is natural that the observed potentials of both cells were not commensurate. In this case we calculated the potentials of the quinhydrone electrodes in the absolute alcohols. The values for E_0 in the absolute alcohols were taken from Br Brodsky's monograph [10].

We shifted the position of the calibration curves to correspond to the difference in potentials between the aqueous saturated calomel electrode and the quinhydrone electrode in absolute alcohol. As is evident from Fig. 4, the calibration curves are situated close to each other. The amount by which the calibration curves differ may be explained by the difference in phase and diffusion potentials. It is quite evident from Fig. 5 that the potentials coincide at the medial pH values for electrode No. 2, made from MacInnes and Dole glass placed in aqueous buffer solutions and in buffer solutions in 88.5% ethyl alcohol. The calibration of the electrodes was conducted under identical conditions. As is evident in this case, the calibration curves coincide at the rectilinear portion.

As a result of these experiments it can again be confirmed that the potential of a glass electrode at medial pH values does not depend upon the medium in which the measurement is conducted.

Acid Region

At the present time there is very little data in the literature on the behavior of the glass electrode in the acid region in aqueous solutions and still less in the acid region in non-aqueous media. We investigated the behavior of glass electrodes in acid and strongly acid regions in water, in ethanol-water mixtures and in absolute ethyl and methyl alcohols. The electrodes made from Yuz glass and from MacInnes and Dole glass were calibrated.

With this aim in mind, hydrochloric acid solutions were prepared in water and in alcohols. The pH of the hydrochloric acid solutions was determined by the hydrogen electrode relative to a standard. As in previous measurements, the standard was a 0.1 N solution of hydrochloric acid in the corresponding medium.

The results for the calibration of glass electrodes in the above solutions of hydrochloric acid are given on Fig. 1 for Yuz glass. As may be observed from Fig. 1, the calibration curve for the electrode has two breaks: a maximum in the alkaline region and a minimum in the acid region. The deviation in the acid region has a reverse sign in relation to the deviation in the alkaline region. It should be noted that in the works on the glass electrode presented in the monographs of Bachelin [11] and Dole [2], mention is made only of the deviation from rectilinearity of the calibration curve in the acid region.

Measurement with a glass electrode in strongly acid solutions is very difficult. The potential is not well established in the extremely acid point of the field. Electrodes made from Yuz glass - wetted for 2-3 days as well as for a longer period of time - give, in all cases, a minimum in the acid region. The position of the minimum then shifts to a less acid region on changing from water to absolute alcohol, which is easily seen from Table 5. As concerns MacInnes and Dole glass, we cannot cite analogous data. Some of the electrodes, wetted for a longer period of time, showed a minimum on the calibration curves. The calibration curves for electrodes prepared a long time before calibration just exhibited a strong deviation from rectilinearity. Even for those electrodes which showed a minimum on the calibration curve, the position of the minimum did not change on varying the solution investigated, and remained at all times at a pH of -0.5.

Shifting the position of the minimum as well as the previously-mentioned deviation of the calibration curve from rectilinearity shorten the rectilinear portion of the calibration curve as the alcohol content increases. In Table 6 is given the relationship of the magnitude of the rectilinear portion of the calibration curve

*The behavior of the glass electrode is practically unknown in strongly acid non-aqueous solutions.

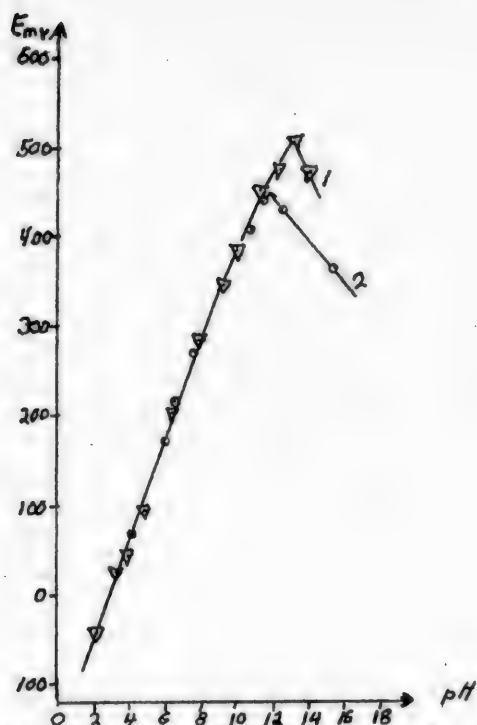


Fig. 5. Calibration curves of a glass electrode made from MacInnes and Dole glass in water and in 88.5% ethyl alcohol.
1 - water; 2 - 88.5% ethyl alcohol.

to the molar fraction of ethyl alcohol in ethanol-water mixtures. The data of Table 6 is represented on Fig. 6.

Available experimental data is still too meager to make general conclusions on the behavior of the glass electrode in the acid region, in particular in an acid region of non-aqueous solutions, but this question deserves attention.

Relationship of the Glass Electrode Potential to the Absolute Acidity

Of especial interest is the representation of our results by the universal scale pA , which is standardized against an infinitely diluted solution of the acid ions in aqueous solution by the use of the average activity coefficient. The universal scale pA , proposed by N.A. Izmailov [12], differs from the pH scale by the value $\lg Y_0$:

$$pA = pH - \lg Y_0,$$

where Y_0 is the average coefficient of the ions at infinite dilution in the given medium, referred to an infinitely diluted aqueous solution of the ions as a standard. The value $\lg Y_0$ for ethyl alcohol is shown in Table 7.

The calibration curves for glass electrodes made from Yuz glass are shown in the pA scale on Figs. 7 and 8 (for acid and alkaline regions respectively). Glass electrodes made from MacInnes and Dole glass give analogous calibration curves, which exhibit a contraction of the minima and maxima in the pA scale.

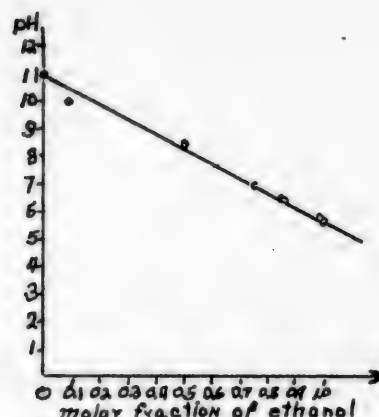


Fig. 6. Relationship of the magnitude of the rectilinear portion of the calibration curve, for the glass electrode made from Yuz glass, to the molar fraction of ethyl alcohol.

TABLE 5

Exp. No.	Solution	pH
1	Water.....	-0.2
2	20% (by wt.) ethanol.	0.0
3	71.9%	+0.3
4	88.5%	+1.2
5	100.0%	+2.2
6	100.0% methanol.....	+1.9

TABLE 6

Exp. No.	Molar fraction of ethanol	Length of the rectilinear portion for Yuz glass in pH units
1	0.0 (water)	10.9
2	0.0891	9.8
3	0.5	8.4
4	0.75	6.9
5	0.85	6.4
6	1.0	5.6

TABLE 7

Exp. No.	Molar fraction of ethanol	log γ_0
1	0.089	0.127
2	0.5	0.597
3	0.75	1.034
4	0.85	1.27
5	1.0	2.32

As may be seen from Fig. 7, on shifting the calibration curve for absolute alcohol to the acid region it approaches a pA value of -1.7. As is evident from the diagrams, the minima and maxima of the calibration curves in different alcohol-water mixtures, using the pA scale, lie along one straight line and tend to coalesce.

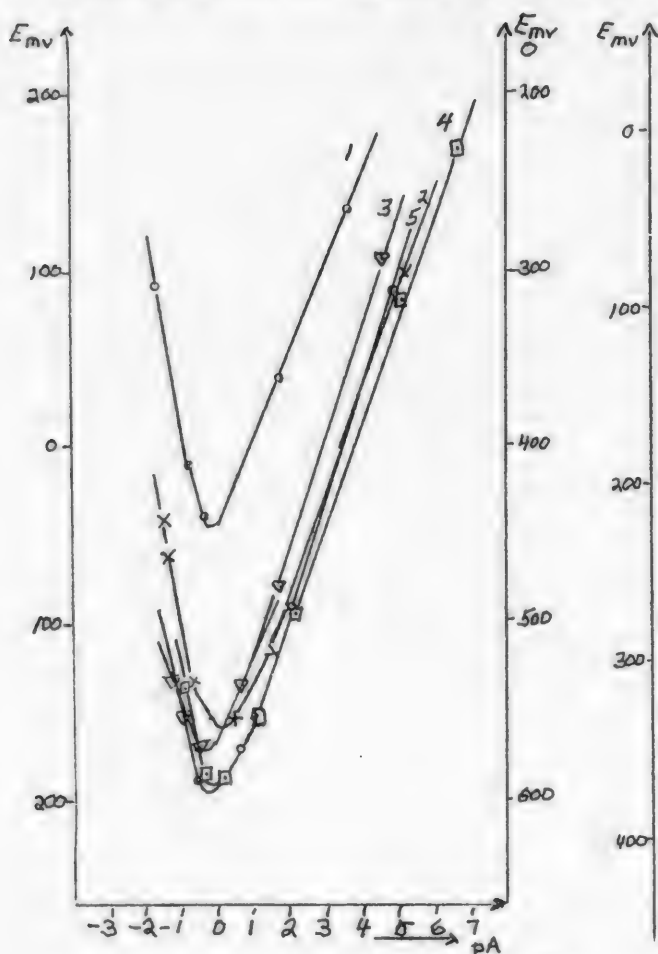


Fig. 7. Calibration curves of glass electrode made from Yuz glass using the universal scale. Acid region. Ethyl alcohol: 1 - 100.0%; 2 - 88.5%; 3 - 71.9%; 4 - 20.0%; 5 - water.

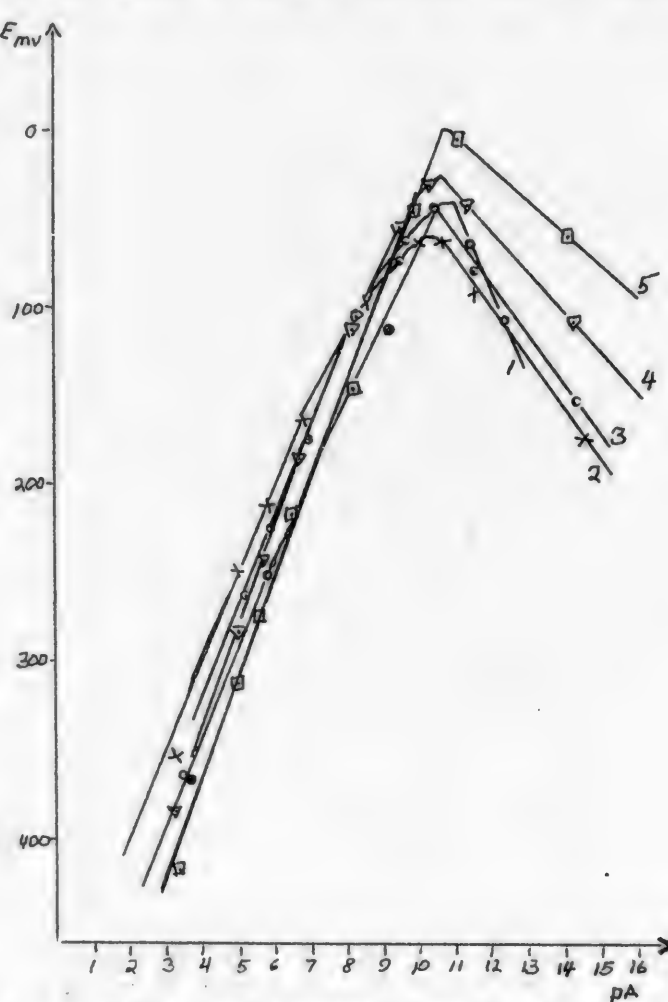


Fig. 8. Calibration curves of a glass electrode made from Yuz glass using the universal scale. Alkaline region. Ethyl alcohol: 1 - 100.0%; 2 - 93.5%; 3 - 88.5%; 4 - 71.9%; 5 - 20.0%.

This consequently indicates that the errors of the glass electrode in acid and alkaline regions are fractions of the total acidity of the medium.

It should be noted that since 1941 we conducted all the experimental work with our own glass furnace.

We wish to take this opportunity to express our deep gratitude to V.A.Pchelin for his kindness in providing us with electrode glass.

SUMMARY

1. An investigation of the behavior of glass electrodes made from Yuz glass and MacInnes and Dole glass was conducted in ethanol-water mixtures and in absolute ethyl and methyl alcohols. It was established that in all these solutions the calibration curve of the glass electrode contains a maximum in the alkaline region. With increase in ethyl alcohol content, the position of the maximum shifts to a more alkaline region.

2. In an acid (hydrochloric acid) region a deviation is observed from the rectilinear potential - solution pH curve, which has a reverse sign to the deviation of the alkaline region, both for aqueous solutions as well as for alcohols. The calibration curve for a glass electrode made from Yuz glass possesses a minimum in the acid region. The position of the minimum, as well as the beginning of deviation from rectilinearity, shifts to a less acid region from water to absolute ethyl alcohol.

3. The value, K , of the exchange constant for glass ions increases on shifting from water to absolute alcohols. If for water, the K of the investigated glasses equals $6.31 \cdot 10^{-13}$, then in absolute ethyl alcohol the K for Yuz glass equals $8.0 \cdot 10^{-7}$ and for MacInnes and Dole glass equals $2.0 \cdot 10^{-7}$. In absolute methyl alcohol the value of K for Yuz glass is equal to $2.82 \cdot 10^{-10}$, and for MacInnes and Dole glass it is equal to $2.82 \cdot 10^{-11}$.

4. The use of the glass electrode for measuring pH in mixtures of ethyl alcohol and water and of absolute ethyl and methyl alcohols is quite practical, but with an increase in the alcohol content the region of applicability of the glass electrode is curtailed.

5. It was shown that the errors of the glass electrode in acid and alkaline regions are situated at the same value of the absolute acidity, pA.

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PHYSICO-CHEMICAL INVESTIGATION OF THE SYSTEM

BENZAMIDE - IODINE CHLORIDE

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Investigations we conducted of the system acetamide - iodine chloride [1] (measurement of electrical conductivity, electrolysis, ion transfer, cyroscopy, etc.) showed that CH_3CONH_2 forms an addition product with ICl , which, however, could not be isolated.

The high electrical conductivity of the system $\text{CH}_3\text{CONH}_2 - \text{ICl}$ is caused by electrolytic dissociation of this compound, the cation of which consists of acetamide and a positively charged ion I^+ , the anion being Cl^- .

The results of this investigation also indicated the possibility of considering the question of the nature of the complex compounds formed by halogens or iodine halogenides (ICl , IBr) with such types of organic compounds as amines, amido acids, ethers, containing electron donors - i.e., nitrogen, oxygen, sulfur atoms, etc.

In the light of these data it was considered of interest to continue the investigation of systems of this type with amides and other acids.

With this purpose in mind we investigated the system benzamide - iodine chloride.

Data in the literature afforded a basis for the belief that benzamide possesses greater complex-forming properties than acetamide in relation to halogens or iodine halogenides.

Thus, whereas any compounds formed from solutions of acetamide in bromine could not be separated, although a physico-chemical investigation of this system led Plotnikova and Yablonsky [2] to conclude the existence of such compounds in a bromine solution of acetamide, the so-called Loran complex $\text{C}_6\text{H}_5\text{CONH}_2 \cdot \text{Br}_2$ has long been known in connection with benzamide.

Results have also been reported for the investigation of the system $\text{C}_6\text{H}_5\text{ONH}_2 - \text{ICl}$ by the methods of thermal analysis, electrical conductivity, cryoscopy, electrolysis and several others.

EXPERIMENTAL

Benzamide was synthesized from "chemically pure" benzoyl chloride and ammonium carbonate [3]. The benzamide so obtained was recrystallized from hot water and carefully dried at 100°C . The melting point of the compound we obtained was 127.3°C .

Iodine chloride was obtained as described in a previous paper [1]. The purification of nitrobenzene was also described there. The methods we used for the investigation have also been described in this paper.

Thermal Analysis

The determination of the solidification point was conducted in the vessel described by Fialkov and Kuzmenko [4] with this difference, that a vertical side-tube containing a platinum agitator was fused to the vessel.

The melting point diagram of the system $\text{C}_6\text{H}_5\text{CONH}_2 - \text{ICl}$ was investigated at concentrations from 0 to 100% benzamide (Table 1 and Fig. 1).

Two eutectics are shown on the melting point curve, at -23°C (98 mol.% ICl) and 23.5° (46.8 mol.% ICl).

The dysetectic point on this curve corresponds to an equimolecular ratio of the components of the system - formation of a compound of the composition $\text{C}_6\text{H}_5\text{CONH}_2 \cdot \text{ICl}$, melting at 36.9° .

This compound, not yet described in the literature, forms needle-like crystals of a dark-yellow color. It is insoluble in water, but is slowly decomposed by water with the liberation of iodine.

Electrical Conductivity of the System $\text{C}_6\text{H}_5\text{CONH}_2 - \text{ICl}$.

The electrolyte was prepared directly in the vessel used for measurement of the electrical conductivity by adding weighed portions of benzamide to the iodine chloride, after which the vessel was kept for some time at 50° until the benzamide completely dissolved.

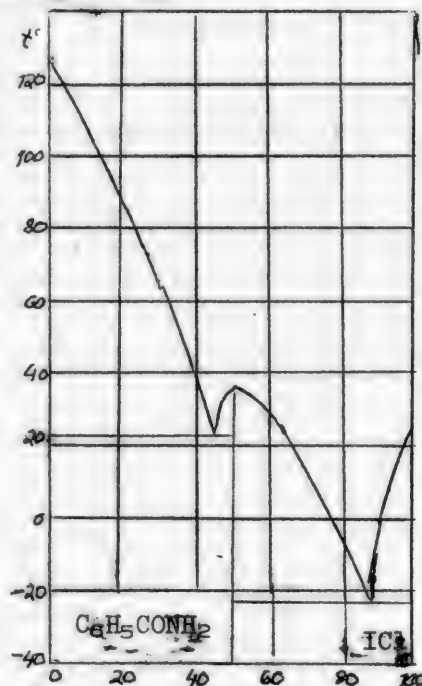


Fig. 1. Melting point curve for the system $\text{C}_6\text{H}_5\text{CONH}_2 - \text{ICl}$.

TABLE 1

Thermal Analysis of the System $\text{C}_6\text{H}_5\text{CONH}_2 - \text{ICl}$

Mol. % $\text{C}_6\text{H}_5\text{CONH}_2$	Temperature intervals		Mol. % $\text{C}_6\text{H}_5\text{CONH}_2$	Temperature intervals	
	First	Second		First	Second
0.00	27.15	—	53.20	27.85	23.10
2.69	21.00	—	53.49	26.55	—
1.10	9.30	—	56.32	24.98	—
9.48	7.10	-23.00	59.09	37.00	23.50
14.23	—	-22.50	63.66	50.30	23.40
21.55	—	-24.90	66.09	—	23.20
31.74	16.50	-23.80	74.72	79.10	—
38.92	27.90	—	85.60	99.50	—
46.23	35.65	—	100.00	127.8	—
50.00	36.90	—			

The electrical conductivity was measured at 35° and at 50° at concentrations from 0 to 61 mol. % of benzamide. Measurements at higher concentrations were not conducted because of the high melting point of the system at these concentrations (at 65° and higher a noticeable decomposition of iodine chloride begins) [5].

The results of the specific electrical conductivity measurements are given in Table 2 and on Fig. 2.

TABLE 2
Specific Electrical Conductivity of the System
 $C_6H_5CONH_2 - ICl$.

$C_6H_5CONH_2$ (mol. %)	$\kappa \cdot 10^3$		Temperature coef- ficient of elec- trical conductivity $\kappa \cdot 10^2$
	35°	50°	
0.00	4.82	5.08	-
4.83	21.47	28.30	2.13
9.17	21.70	29.64	2.43
11.88	20.80	27.45	2.13
14.08	17.42	25.28	-
21.17	13.08	17.71	2.35
30.22	5.67	9.58	4.87
33.49	3.62	7.77	7.61
46.28	1.47	3.16	8.05
50.81	-	2.43	-
44.19	0.92	1.97	7.60
60.87	-	1.79	-

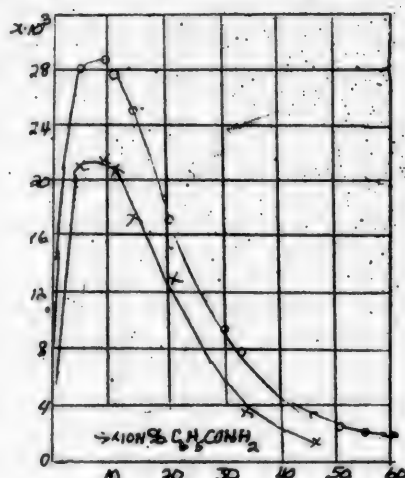


Fig. 2. Specific electrical conductivity of the system
 $C_6H_5CONH_2 - ICl$.

The specific electrical conductivity of the system $C_6H_5CONH_2 - ICl$ first increases sharply on adding benzamide and then reaches a maximum (0.03 mhos at 50°) at a benzamide concentration of ~ 10 mol. %, then falls and at 35 mol. % $C_6H_5CONH_2$ the electrical conductivity of iodine chloride decreases.

The change of the temperature coefficient of electrical conductivity with concentration is shown on Fig. 3.

A sharp jump in the temperature coefficient of the system is seen on this curve at a concentration region of about 30 mol. %, $C_6H_5CONH_2$, and a maximum at about 50 mol. % of benzamide.

The specific gravity of the system $C_6H_5CONH_2 - ICl$ (Table 3 and Fig. 4) was determined in order to calculate the molecular electrical conductivity.

The specific gravity isotherm exhibits a small break at about 45 mol. % benzamide.

We calculated the molecular electrical conductivity in two ways, taking ICl (I) or $C_6H_5CONH_2$ (II) as an electrolyte (see Table 4 and Fig. 5).

Based on ICl as an electrolyte, the molecular electrical conductivity isotherm has an "anomalous" character. The second isotherm exhibits an increase in electrical conductivity with dilution.

It should be noted that there is a considerable analogy with the system $CH_3CONH_2 - ICl$ [1] as concerns the relationship of the specific and molecular electrical conductivity of the system $C_6H_5CONH_2 - ICl$. The appearance of the electrical conductivity curves of both systems is evidence of the occurrence of complex formation.

Electrical Conductivity of the System $C_6H_5CONH_2 - ICl$ in a Solution of Nitrobenzene

These experiments were conducted in order to elucidate the electrochemical properties of the system $C_6H_5CONH_2 - ICl$ in solution, the behavior of the complex formed

in this system, the nature of the complex ions in the solution, etc.

With this in mind, cryoscopic investigations and electrolysis experiments were conducted. These will be described later.

To determine the electrical conductivity of the nitrobenzene solutions, iodine chloride was first added to a weighed amount of nitrobenzene contained in the measurement vessel. Then separate increments of benzamide were added, gradually increasing its concentration up to the ratio $C_6H_5CONH_2:ICl$ and a little above. Further additions could not be made because of the limited solubility of benzamide in a nitrobenzene solution of iodine chloride. The results of the determinations are shown in Table 5 and on Fig. 6.

The electrical conductivity of nitrobenzene solutions is approximately 10 times less than the electrical conductivity of the binary system. A flat maximum is observed on the electrical conductivity isotherms. By comparing the electrical conductivity of solutions of the first and second series, it is evident that this maximum shifts in the direction

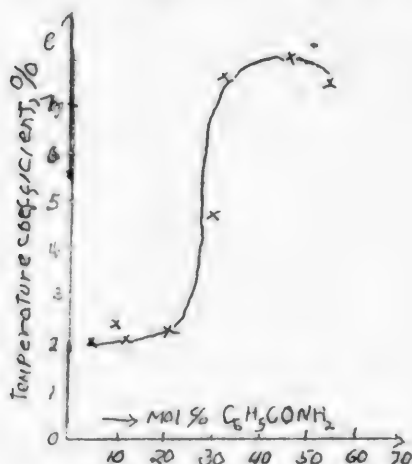


Fig. 5. Temperature coefficient of electrical conductivity of the system $C_6H_5CONH_2 - ICl$

of iodine chloride on increasing the concentration of ICl in nitrobenzene: in the first series of experiments the electrical conductivity maximum approximately corresponds to an equimolecular ratio when the ratio $ICl:C_6H_5NO_2$ was equal to 1:3.39.

In the second stage of experiments the electrical conductivity maximum approaches 30 mol. % of benzamide at a $ICl:C_6H_5NO_2$ ratio of 1: 1.89.

TABLE 3

Specific gravity of the System $C_6H_5CONH_2 - ICl$

Mol. % $C_6H_5CONH_2$	Sp. gr. at 50°
0.00	3.166
4.93	2.966
6.29	2.923
9.30	2.840
12.86	2.780
17.28	2.581
18.88	2.520
20.33	2.512
21.88	2.416
26.52	2.333
28.70	2.227
34.71	2.092
42.43	1.953
44.26	1.920
50.35	1.854
54.37	1.785
57.72	1.747

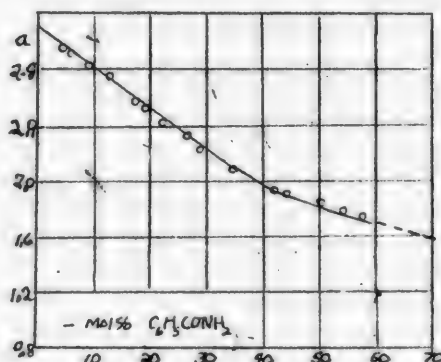


Fig. 4. Specific gravity of the system $C_6H_5CONH_2 - ICl$.

TABLE 4

Molecular conductivity of the system $C_6H_5CONH_2 - ICl$ at 50° .

Mol. % ICl	ϕI (in ml)	κ_I	Mol. % ICl	ϕII (in ml)	κ_{II}
100.00	51.3	0.50	-	-	-
95.13	56.3	1.60	4.87	1109.0	31.45
90.83	60.9	1.81	9.17	605.2	17.95
88.12	64.3	1.77	11.88	477.2	13.10
85.92	67.0	1.79	14.08	409.1	10.34
78.83	78.0	1.58	21.17	291.6	5.16
69.78	46.6	0.43	30.22	223.1	2.14
66.51	104.6	0.81	33.49	207.9	1.62
53.72	138.9	0.44	46.28	162.0	0.51
49.19	154.8	0.38	50.81	150.0	0.36
45.05	172.2	0.34	54.95	141.2	0.28
39.13	204.8	0.37	60.87	127.5	0.25

TABLE 5

Specific conductivity of the System
 $C_6H_5CONH_2 - ICl - C_6H_5NO_2$

ICl $C_6H_5NO_2$ (moles)	$C_6H_5CONH_2$ ICl (moles)	Specific electrical conductivity $\times 10^4$
		25°

First series

1 3.39	0	4.56	5.08
	0.114	19.52	25.05
	0.233	25.19	31.50
	0.317	28.47	35.14
	0.472	29.75	35.91
	0.638	30.30	36.70
	0.998	28.11	36.20
	1.188	25.97	35.67
	1.500	25.39	30.97

Second series

1 1.89	0	9.14	11.20
	0.027	21.64	25.85
	0.113	34.43	43.81
	0.215	39.77	49.64
	0.270	40.26	52.65
	0.440	20.77	52.92
	0.631	35.37	46.55
	0.965	29.67	38.66
	1.343	25.63	

the solubility of benzamide in a nitrobenzene solution of ICl, we took into account (deducted), that quantity of $C_6H_5CONH_2$ which should have dissolved in the weight of nitrobenzene, i.e., its true solubility.

The given solution was saturated with respect to benzamide.

Solubility of Benzamide in a Nitrobenzene Solution of Iodine Chloride

Qualitative experiments showed that benzamide, which is slightly soluble in nitrobenzene, dissolves to a greater extent in the presence of iodine chloride. The color of the ICl solutions in nitrobenzene is considerably weakened by solution of the benzamide.

The solubility determination was conducted in the following fashion: to a solution of ICl in nitrobenzene contained in a flask with a ground-glass stopper, an excess of benzamide was added (but in Experiment 4, Table 6, an insufficient quantity of benzamide was taken for the solution). The flask was kept at 20° for 4-5 hours, with frequent shaking. The undissolved benzamide was then filtered by suction through a glass filter funnel closed with a stopper fitted to a calcium chloride tube, washed with a small quantity of ether, dried and weighed. In calculating

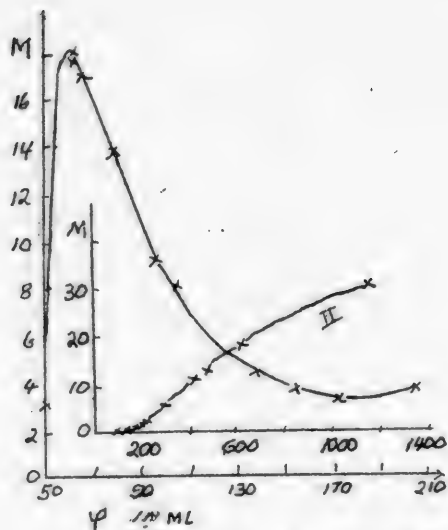


Fig. 5. M_I - ICl taken for the electrolyte. M_{II} - $C_6H_5CONH_2$ taken for the electrolyte.

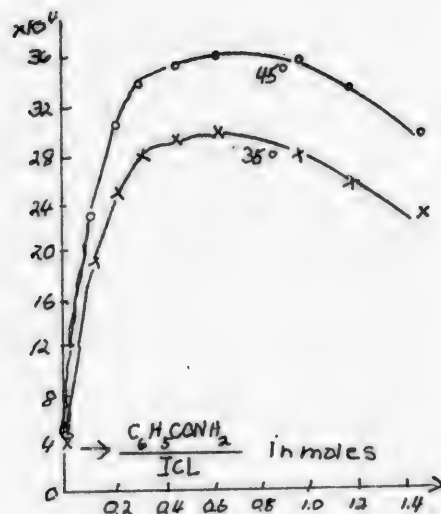


Fig. 6. Specific electrical conductivity of the system $C_6H_5CONH_2$ - ICl - $C_6H_5NO_2$.

TABLE 6

Solubility of Benzamide in a Nitrobenzene Solution of ICl

Exp. No.	Weight of nitrobenzene (g)	Weight of iodine chloride (g)	Weight of benzamide (g)	Solubility of benzamide (g)	Molar ratio in the solution: $\frac{C_6H_5CONH_2}{ICl}$
1	5.9959	-	1.0015	0.1123	-
2	6.0034	0.8123	1.0015	0.7732	1.09
3	5.9840	1.1613	0.9742	0.9721	0.99
4	5.9885	3.2692	1.0015	1.0015	-
5	5.9885	3.2692	3.0616	2.9401	1.16

As is evident from the data of Table 6, the solubility of $C_6H_5CONH_2$ in a nitrobenzene solution of ICl (in absolute quantities) increases with an increase in the concentration of iodine chloride. But, notwithstanding the rather wide range of ICl concentrations in our experiments, from 0.103 to 0.42 moles of ICl for each mole of $C_6H_5CONH_2$, the ratio of the quantity of dissolved $C_6H_5CONH_2$ to the quantity of ICl in solution is very close to equimolecular - on the average, 1.08 moles of $C_6H_5CONH_2$ for each mole of ICl.

This fact proves the formation, in a nitrobenzene solution, of a complex compound of iodine chloride and benzamide of the composition $C_6H_5CONH_2 \cdot ICl$.

Cryoscopic Investigations of the System $C_6H_5CONH_2$ - ICl in a Solution of Nitrobenzene

These investigations were conducted by the Beckmann method.

The results of these determinations are given in Table 7 and on Fig. 7. In the table: t^0 is the freezing point of nitrobenzene, t_1 of the nitrobenzene solution of ICl, t_2 of the nitrobenzene solution of ICl and $C_6H_5CONH_2$; Δt_1 is the

lowering of the freezing point effected by iodine chloride; Δt_2 is the depression observed upon addition of $C_6H_5CONH_2$ to the solution of ICl in nitrobenzene ($t_1 = t_2$).

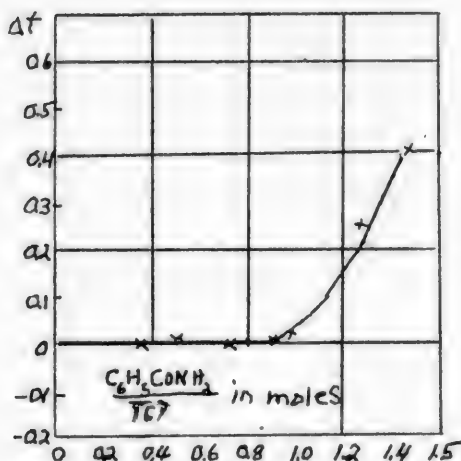


Fig. 7. Cryoscopy of the system $C_6H_5CONH_2$ - ICl in nitrobenzene.

As is evident from the data obtained, the addition of benzamide up to an equimolecular ratio of ICl either does not change the freezing-point depression or increases it only very slightly. Only after increasing the equimolecular ratio $C_6H_5CONH_2:ICl$ is there observed a sharp increase in the freezing-point depression of the solution, caused by excess $C_6H_5CONH_2$ molecules not entering into the composition of the complex: $C_6H_5CONH_2 \cdot ICl$.

This may also be confirmed in the following fashion: if the excess quantity of benzamide in Experiments 8 and 9 is calculated, and if it is assumed that the depression Δt observed in these experiments is caused by this quantity of benzamide, and if the molecular weight of the latter is then calculated, a value is obtained which is very close to the theoretical. Thus, for example, according to the data of Experiment 8, we obtain:

$$M_{C_6H_5CONH_2} = \frac{0.092 \cdot 6.89 \cdot 1.000}{18.2592 \cdot 0.260} = 135.20.$$

TABLE 7

Cryoscopy of the System $C_6H_5CONH_2$ - ICl in Nitrobenzene

Exp. No.	Weight of $C_6H_5NO_2$ (g)	Weight of ICl (g)	Weight of $C_6H_5CONH_2$ (g)	$\frac{C_6H_5CONH_2}{ICl}$ (in moles)	t_0	t_1	t_2	Δt_1	Δt
1	18.2592	0.4736	—	—	4.825	—	—	—	—
2			—	—	—	3.860	—	0.965	—
3			0.1261	0.357	—	—	3.865	—	0.005
4			0.1854	0.525	—	—	3.840	—	0.020
5			0.2566	0.727	—	—	3.860	—	0.000
6			0.3191	0.904	—	—	3.845	—	0.015
7			0.3391	0.961	—	—	3.835	—	0.025
8			0.4454	1.262	—	—	3.600	—	0.260
9			0.5166	1.463	—	—	3.450	—	0.410

The formula molecular weight of $C_6H_5CONH_2 = 121.05$.

If the molecular weight of the complex $C_6H_5CONH_2 \cdot ICl$ is calculated from the data of experiment 7, in which the ratio $C_6H_5CONH_2:ICl$ was very close to equimolecular, then 314.8 is obtained:

The total solubility of benzamide was taken to calculate this ratio.

$$M = \frac{0.8127 \cdot 6.89 \cdot 1000}{18.2592(4.825 - 3.835)} = 309.8.$$

The theoretical molecular weight of this complex is 283.43. These data indicate that the complex $C_6H_5CONH_2 \cdot ICl$ is in an associated condition in nitrobenzene solution.

Although the apparent association factor of the investigated complex is relatively small, if it is considered that the electrical conductivity of nitrobenzene solutions of the complex at a given concentration is rather high ($3-4 \cdot 10^{-3}$ mhos), it may then be postulated that the actual association factor of the complex $C_6H_5CONH_2 \cdot ICl$ is equal to two.

Of course, this does not exclude the possibility that the associated molecules of the complex are in equilibrium with the monomolecular molecules.

Electrolysis and Ion Transfer

These experiments were conducted in a vessel with three sections as in the investigation of a nitrobenzene solution of the complex $C_6H_5N \cdot ICl$ [6].

The cathode used was platinum, the anode was silver and covered with a layer of a silver halogenide. In order to maintain a constant temperature during electrolysis a portion of the apparatus was submerged in a thermostat.

To prepare the electrolyte, an equimolar quantity of $C_6H_5CONH_2$ was added to a nitrobenzene solution of ICl .

In several experiments the electrolyte was prepared in the following fashion: First, the complex $C_6H_5CONH_2 \cdot ICl$ was obtained by fusing equimolar quantities of $C_6H_5CONH_2$ and ICl . This was then dissolved in nitrobenzene. In both cases identical results were obtained.

The duration of the electrolysis was 24 - 100 hours, the current from 3 to 1 mA.

In all the electrolysis experiments it was found that benzamide shifted to the catholyte and precipitated on the cathode as rectangular, colorless (after washing with nitrobenzene) platelets.

During the first several hours of electrolysis the color of the catholyte became continuously darker, which was caused by an initial transfer of I^+ ions to the cathode and their separation as molecular iodine. Several hours after the beginning of the electrolysis the color of the catholyte became less intense and the color of the anodic liquid began to darken simultaneously. It thus follows from these experiments that in the electrolysis of the complex $C_6H_5CONH_2 \cdot ICl$ in a nitrobenzene solution (as with the investigation of the systems $CH_3CONH_2 \cdot ICl$ and $C_5H_5N \cdot ICl$) the molecules of the organic substance contained in the complex cation, which also contains iodine, are transferred to the cathode where they are liberated after discharge of the cations.

In order to characterize the electrolysis of the system $C_6H_5CONH_2 \cdot ICl - C_6H_5NO_2$ quantitatively, analyses of the cathodic, anodic, and intermediate liquids were conducted. Methods for the quantitative determination of benzamide, iodine, and chlorine are the same as with the investigation of the system $CH_3CONH_2 \cdot ICl - C_6H_5NO_2$ [1].

The analytical results for the cathodic and anodic liquids are given in Tables 8 and 9.

The content of $C_6H_5CONH_2$, iodine and chlorine in the intermediate liquid changed very slightly. Therefore these data are not given in the tables.

TABLE 8

TRANSFERENCE OF CHLORINE AND IODINE IN A NITROBENZENE SOLUTION OF $C_6H_5CONH_2 \cdot ICl$

Exp. No.	Conc. of $C_6H_5CONH_2 \cdot ICl$ (in mol %)	Copper separated in the coulomb meter		Should contain(g)		Found (g)		Difference (in g)		Increase in weight of the anode	I:Cl ratio (in g-atoms) after electrolysis	Milliequivalents transferred by the current	
				iodine	chlorine	iodine	chlorine	iodine	chlorine			iodine	chlorine
1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	9.76	0.0230	anolyte	0.4667	0.1304	0.5712	0.1524	+0.1045	+0.0220	0.0416	0.64	0.823	1.796
			catholyte	0.5365	0.1499	0.4315	0.0851	-0.1050	-0.0638		1.11	0.827	1.797
2	9.76	0.0163	anolyte	0.4315	0.1205	0.5331	0.1517	+0.1016	+0.0312	0.0170	0.98	0.800	1.358
			catholyte	0.5409	0.1511	0.4316	0.0957	-0.1033	-0.0554		1.26	0.8605	1.561
3	9.17	0.0292	anolyte	0.4327	0.1265	0.6038	0.1418	+0.1566	+0.0154	0.0546	0.68	1.233	1.972
			catholyte	0.6053	0.1691	0.4443	0.0939	-0.1610	-0.0651		1.03	1.267	1.834
4	9.17	0.0326	anolyte	0.4148	0.1158	0.6044	0.1418	+0.1896	+0.0260	0.0705	0.62	1.493	2.718
			catholyte	0.5134	0.1434	0.3237	0.0497	-0.1897	0.0337		1.42	1.493	2.639
5	11.54	0.0348	anolyte	0.7402	0.2068	0.8726	0.2837	+0.1324	+0.0769	—	0.86	1.043	1.982
			catholyte	0.7010	0.1958	0.5712	0.1196	-0.1298	-0.0762		1.33	0.934	1.963

* In this experiment a platinum anode and cathode were used.

TABLE 9

TRANSFERENCE OF BENZAMIDE IN A NITROBENZENE SOLUTION OF $C_6H_5CONH_2 \cdot ICl$

Exp. No.		Should contain benzamide (g)	Found benzamide (g)	Difference
2	anolyte	0.4145	0.3874	-0.0271
	catholyte	0.5195	0.5567	+0.0372
3	anolyte	0.4319	0.3833	-0.0486
	catholyte	0.5774	0.6255	+0.0481
4	anolyte	0.3957	0.3025	-0.0932
	catholyte	0.4898	0.6053	+0.1152
	anolyte	0.7131	0.5544	-0.1587
5	catholyte	0.6753	0.8025	+0.1278

In Table 8 the gain in weight of the anode after electrolysis is also shown. The platinum cathode did not change in weight.

The results of these experiments confirm the fact that hexanide is transferred to the catholyte (Table 9), and chlorine = to the anolyte (Table 8).

It may be postulated that the precipitate at the anode consists principally of silver chloride.

Thus, if the gain in weight of the anode (column 11, Table 8) is combined with the excess chlorine found in the anolyte (column 10), a value is obtained which is very similar to the quantity of chlorine which was transferred from the catholyte to the anolyte.

As concerns iodine, the fact that the iodine content as well as the chlorine content increases in the anodic portion of the solution does not refute the conclusion drawn earlier on the initial transfer of iodine to the cathode.

What conclusions may be drawn on the composition of the ions based on these experiments?

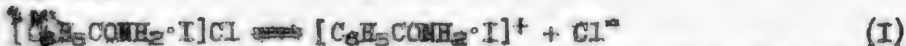
To answer this question, it must be borne in mind that according to the results of the cryoscopic measurements, the complex $C_6H_5CONH_2 \cdot ICl$ is associated in a nitrobenzene solution.

We postulated that the association factor is equal to two and that the associated molecules are in equilibrium with the monomeric molecules of this complex.

It must also be considered that the number of equivalents of iodine and chlorine transferred to the anolyte in the same experiment are in a ratio of 1:1.5 to 1:2 (Table 8).

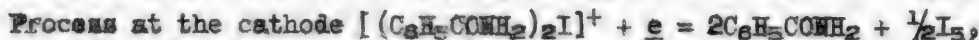
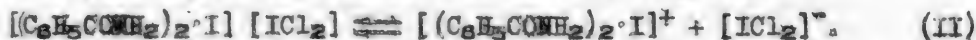
From all these factors the following conclusions may be drawn:

For monomeric molecules the complex $C_6H_5CONH_2 \cdot ICl$ follows the same scheme of electrolytic dissociation and possesses the same ionic nature as the system $CH_3CONH_2 \cdot ICl$ [1], that is:



For dimeric molecules a structure represented by the formula $[(C_6H_5CONH_2)_2 \cdot I][ICl_2]$ is considered possible.

The electrolytic dissociation of such molecules and the phenomena taking place upon electrolysis may be represented in the following way:



In Table 10 is shown the quantity of chlorine and iodine which should be transferred to the anolyte in accordance with the readings of the coulomb meter, assuming that the passage of 1F corresponds to the transfer of one gram-ion of ICl_2 .

The amount of chlorine and iodine so calculated is for the most part similar to that obtained by the experimental means (Table 8).

These facts confirm our postulate on the presence of dimeric molecules of the

complex $C_6H_5CONH_2 \cdot ICl$ and their electrolytic dissociation according to the above-presented scheme (II).

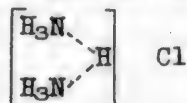
The fact that after electrolysis the ratio I:Cl increases in the catholyte and decreases in the anolyte, agrees both with scheme (I) on the dissociation of monomeric molecules and with scheme (II) on the dissolution of the associated molecules of the complex $C_6H_5CONH_2 \cdot ICl$.

Iodine, which separates at the cathode by discharge of the complex cations may then be partially transferred to the anode, as was observed with the electrolysis of the system $\text{CH}_3\text{CONH}_2 - \text{I}_2$, due to the electrolytic dissociation of the complex compound of benzamide and iodine, which is probably formed during electrolysis in the system we investigated.

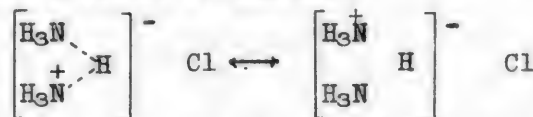
The second process (transfer of iodine to the anolyte) explains the fact that in a series of experiments the quantity of iodine transferred to the anolyte reaches a ratio of 1.5 equivalents of iodine for every 2 equivalents of chlorine.

In relation to its structure the cation $[(C_6H_5CONH_2)_2I]^+$ must be compared to the so-called "anomalous" ammonium salts, for example $2NH_3 \cdot HCl$: in both cases one H^+ or I^+ electron acceptor is combined with two electron donors.

Werner proposed the following structure for the complex $2\text{NH}_3 \cdot \text{HCl}$.



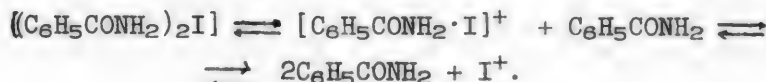
Evidently, in compounds of this type a resonance of the two structures exists, wherein each of the protons (or other acceptor of electrons) forms a bond with one molecule of NH_3 due to the van der Waal reaction, and an ammonium (or "onium") bond with the other molecule of ammonia:



From these considerations, we deem it possible that the structure of the cation $[(C_6H_5CONH_2)_2I]^+$ may be represented in the following fashion:



In concluding this paper it should also be noted that the complex cations $[(C_6H_5CONH_2)_2I]^+$ may undergo stepwise dissociation and be in equilibrium with less complex cations (with a lesser degree of solvation), and even with the simple cations I^+ :



This probably explains the fact that we did not obtain more or less definite and constant values for the electrolytic transfer of benzamide. In our experiments, 0.5 to 2 g-molecules of benzamide are required for 1 g-equivalent of iodine transferred to the anolyte (if it is assumed that F corresponds to the transfer of two

TABLE 10

Expt. No	Copper separated in the coulomb meter	Should be transferred to the anolyte chlorine, g iodine, g	
1	0.0230	0.0513	0.0918
2	0.0163	0.0361	0.0651
3	0.0292	0.0651	0.1170
4	0.0326	0.0727	0.1302

moles of $C_6H_5CONH_2$).

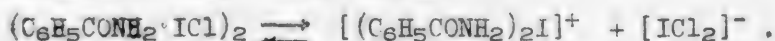
SUMMARY

1. The system benzamide - iodine chlorine was shown, by the thermal analysis method, to form a compound $C_6H_5CONH_2 \cdot ICl$ thus far not described in the literature.

2. The high specific electrical conductivity of the system $C_6H_5CONH_2 - ICl$, reaching a value of 0.03 mhos at 50° , is caused by an electrolytic dissociation of this complex.

3. This complex is also formed in a nitrobenzene solution of the system $C_6H_5CONH_2 - ICl$. This was shown by experiments on the solubility of benzamide in a nitrobenzene solution of iodine chloride and by cryoscopic measurements. The results of these measurements afford a basis for the postulation that in nitrobenzene solutions the complex $C_6H_5CONH_2 \cdot ICl$ is also found in an associated state - as dimeric molecules.

4. An electrolytic study of the transfer of the ions of the complex $C_6H_5CONH_2 \cdot ICl$ in a nitrobenzene solution showed that the dimeric molecules of this complex dissociate to ions according to the scheme:



The monomeric molecules should have the same structure, $(C_6H_5CONH_2 \cdot I)Cl$ as the complex formed in the system $CH_3CONH_2 - ICl$.

5. The structure of the cation $[(C_6H_5CONH_2)_2 \cdot I]^+$ was discussed.

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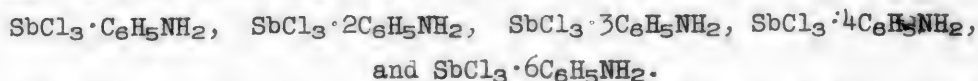
THE ELECTRICAL CONDUCTIVITY OF THE SYSTEM

ANILINE-ANTIMONY TRICHLORIDE

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This system was studied by Menshutkin [1] by the method of thermal analysis. He found that the following compounds of antimony chloride and aniline were present:



Three of these compounds ($\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{NH}_2$, $\text{SbCl}_3 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$, and $\text{SbCl}_3 \cdot 3\text{C}_6\text{H}_5\text{NH}_2$) melted without noticeable decomposition. In addition to the melting point, Kurnakov [2] studied the viscosity of the system. The viscosity isotherms led through a maximum at 50 mol.%, indicating the formation of only one compound - $\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{SbCl}_3$. The results of the viscosity and melting point investigations thus show that this is an example of the systems for which the evidence of the diagrams of different properties is in conflict. The melting point diagram indicates the presence of five compounds in the system; the viscosity curve reflects the presence of only a single thermally more stable compound. A phenomenon of this same kind can be observed in the investigations of other authors [3]. The divergence in the indications is observed not only for the diagram of the properties mentioned, but for others as well, for example, in the diagrams of viscosity and electrical conductivity, where the divergence is seen not only with regard to the number of compounds, but with regard to their composition as well. Thus, the viscosity isotherm of the system pyridine-arsenic trichloride, investigated by Kondratenko [4], indicates that the equimolecular compound $\text{C}_5\text{H}_5\text{N} \cdot \text{AsCl}_3$ is formed in the system, while the minimum of the electrical conductivity isotherm, obtained by Kozmina [5], corresponds to a compound with a different composition $2\text{C}_5\text{H}_5\text{N} \cdot \text{AsCl}_3$. The composition of the first of these compounds corresponds only to a point of inflection on the curve of the temperature coefficient of electrical conductivity. Consequently, the compound formed in the system does not exert a completely uniform influence according to one or the other composition on the course of the curve, and whereas one compound is reflected in the diagram of one property, it is fully possible that another compound may be observed only in the study of some other property.

In the opinion of M.I. Usanovich [6], the curve for the temperature coefficient of electrical conductivity indicates the composition of the compounds formed in the system.

It was of interest to investigate whether the curves of the system antimony chloride - aniline, observed by thermal analysis, were reflected in the diagrams of electrical conductivity and its temperature coefficient.

EXPERIMENTAL

The substances investigated were carefully purified and kept in sealed ampoules. The aniline was first dried with caustic potash, then over metallic sodium, above which it was distilled. A fraction with boiling point 180-181° at

752 mm, was taken for study. The antimony trichloride was prepared from the pentachloride by reduction with metallic antimony. The antimony trichloride thus obtained was purified by distillation followed by fractional solidification in sealed ampoules. The melting point of the SbCl_3 was 73.3° .

The electrical conductivity was measured by the usual Kohlrausch method at 65° and at the same temperatures (95° and 125°) at which the viscosity of the system had been studied, in order to permit comparison of our data and those of other authors.

The results of the measurement of the specific electrical conductivity of the system $\text{SbCl}_3 - \text{C}_6\text{H}_5\text{NH}_2$ and the values of the relative temperature coefficient are given in Table 1, and shown graphically in Figs. 1 and 2.

Fig. 1 shows that the specific electrical conductivity isotherms have a form similar to that of the isotherms of specific electrical conductivity obtained by M. Usanovich [7] and F. Terpuhov [8] for the system $\text{AsCl}_3 - (\text{C}_2\text{H}_5)_2\text{O}$.

In the region of high antimony chloride content (Fig. 1), the curves lead through a maximum, at 125° reaching a very high value (order of $2 \cdot 10^{-2}$ reciprocal ohms).

With change in temperature, the curves of specific electrical conductivity undergo deformation. The point of inflection of the 125° isotherm gradually disappears as the temperature is lowered, and at 65° is converted into a diffused

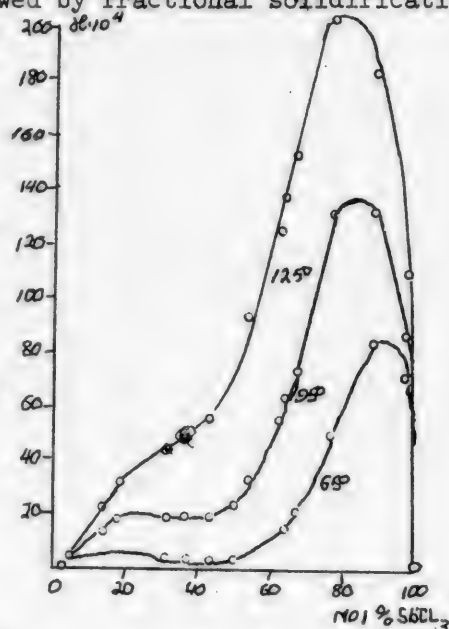


Fig. 1. Isotherms of the specific electrical conductivity.

TABLE 1

Mol. % SbCl_3	Electrical conductivity $\kappa \cdot 10^{-4}$			$C \cdot 10^{-3}$ 95 - 125
	65°	95°	125°	
2.72	-	1.441	1.338	-2.38
4.44	2.863	2.672	3.780	13.82
13.52	-	14.453	33.265	20.32
18.07	-	18.110	32.450	26.39
31.15	4.907	19.460	44.070	42.15
36.60	3.658	19.790	49.000	49.34
42.75	2.832	19.560	55.930	61.98
49.57	4.065	23.710	74.27	71.08
53.58	-	32.67	93.94	62.51
61.79	13.42	55.52	125.10	41.78
63.35	14.63	62.62	139.60	40.98
66.54	20.84	73.86	154.10	36.21
76.15	48.88	132.08	203.50	18.02
87.75	83.89	132.70	183.90	12.86
96.69	72.50	87.58	110.30	8.52

minimum, situated near 50 mol.%. This fact is to some extent an indication of the formation of a molecular compound by the components of the system.

The curve of the temperature coefficient of electrical conductivity (Fig. 2) passes through a maximum at 50 mol.%, and in the region of high acetic acid content has a more complicated form. This, apparently, is explicable by the formation in the system of unstable compounds.

In order to investigate the electrical conductivity curve without dependence upon the viscosity we utilized the data of Krotkov, and eliminated the influence of this factor. The results of the calculation are given in Table 2 and depicted graphically in Fig. 3. From this figure it is clear that the isotherms of corrected electrical conductivity run along smoothly, thus showing the essential influence of the viscosity on the course of the isotherms of electrical conductivity which are thus greatly distorted.

TABLE 2

Mol.% SbCl ₃	Corrected electrical conductivity	
	95°	125°
2.72	0.000001585	0.0000003479
4.44	0.000003741	0.000001210
13.52	0.00004191	0.00001163
18.07	0.0001087	0.00002336
31.15	0.0002277	0.00006610
35.60	0.0003701	0.0001029
42.75	0.0005672	0.0001566
49.57	0.0008962	0.0002599
53.58	0.001202	0.0003382
61.79	0.001321	0.0003878
63.35	0.001315	0.0004050
66.54	0.001300	0.0004160
76.15	0.001109	0.0003866
87.75	0.0004909	0.0002207
96.69	0.0001752	0.00008102

Figs. 4 and 5 give the isotherms of the molecular electrical conductivity, for whose calculation the values of the density were also taken from the work of Krotkov. The curve of molecular electrical conductivity (Fig. 4) calculated for SbCl₃ as electrolyte (Table 3) has a sharply anomalous character, apparently confirming the fact that in these solutions the electrolytes are complex compounds formed by the interaction of the components of the system [9,10]. As is indicated in Fig. 4, in the region of little dilution, the curve of molecular electrical conductivity rises sharply, then immediately takes a sharp downward plunge, then rises again and drops again, but more slowly, thus showing 2 maxima.

The isotherms of molecular electrical conductivity calculated for aniline as electrolyte, are given in Fig. 5, and the data for them are listed in Table 4. The

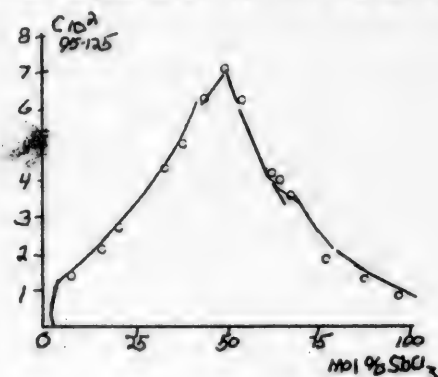


Fig. 2. Temperature coefficient of electrical conductivity.

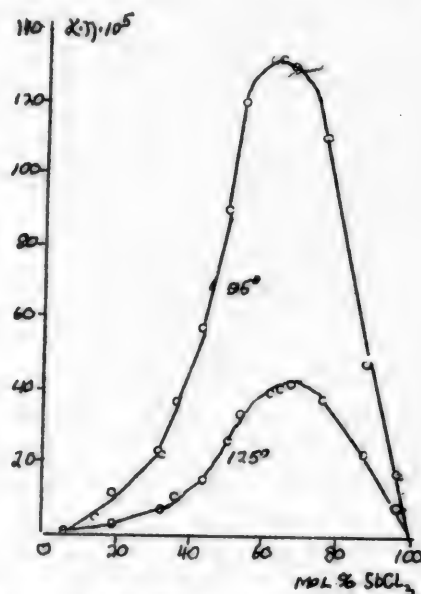


Fig. 3. Isotherms of corrected electrical conductivity.

TABLE 3

Weight % SbCl_3	v_{95°	μ_{95°	v_{125°	μ_{125°
6.52	3498	0.5040	3544	0.4876
10.22	2167	0.5790	2254	0.8522
27.70	686.3	0.9919	709.9	1.6510
35.10	507.7	0.9195	524.1	1.7010
52.58	283.6	0.5518	291.2	1.2830
57.54	243.2	0.4813	250.9	1.2290
64.66	201.6	0.3943	206.3	1.1540
70.66	171.7	0.4071	176.4	1.3100
73.88	157.5	0.5346	162.5	1.5260
79.86	136.0	0.7552	140.0	1.7520
80.92	132.3	0.8287	136.2	1.9010
82.97	126.7	0.9358	130.9	2.017
88.67	110.4	1.4580	113.8	2.316
94.83	96.60	1.2820	96.60	1.777
98.62	88.90	0.7791	91.42	1.245

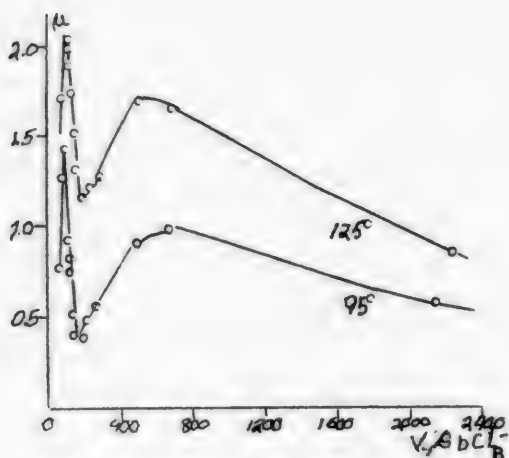
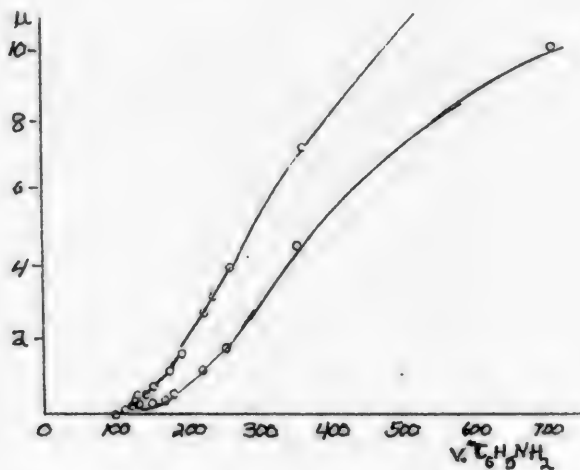
Fig. 4. Molecular electrical conductivity calculated for SbCl_3 as electrolyte.Fig. 5. Molecular electrical conductivity calculated for $\text{C}_6\text{H}_5\text{NH}_2$ as electrolyte.

TABLE 4

v_{95°	μ_{95°	v_{125°	μ_{125°	v_{95°	μ_{95°	v_{125°	μ_{125°
99.55	0.01435	103.7	0.01388	181.80	0.5939	187.5	1.762
100.60	0.02689	104.7	0.03958	220.00	1.2220	226.5	2.834
107.30	0.15500	110.0	0.2581	229.00	1.4340	235.6	3.289
112.00	0.20290	115.6	0.3752	251.80	1.8600	260.2	4.010
128.30	0.2460	131.7	0.5804	352.50	4.6530	363.4	7.395
134.50	0.26610	138.7	0.6797	722.90	9.5930	743.8	13.680
150.50	0.29430	154.0	0.8613	2594	22.72	2665	36.300
168.70	0.40000	173.3	1.2870				

curve of Fig. 5 has a less anomalous character, rising smoothly with greater dilution along almost its entire length.

From the experimental data given, it follows that both in the diagrams of specific electrical conductivity and of the temperature coefficient there is a reflection of the presence of only one more stable compound of the composition $C_6H_5NH_2 \cdot SbCl_3$, while, judging from the diagram of melting points by Menshutkin, we should expect the indication of still another comparatively stable compound ($SbCl_3 \cdot 2C_6H_5NH_2$), especially on the curve of the temperature coefficient of electrical conductivity, on which the results of the chemical interaction of the components of the system appear more completely and more sharply. All the other compounds indicated by thermal analysis give no "special" points on these diagrams, and only slightly complicate the course of the curves.

SUMMARY

1. The electrical conductivity of the system $SbCl_3 - C_6H_5NH_2$ has been studied at 65, 95, and 125°.
2. The molecular conductivity calculated on the basis of $SbCl_3$ as electrolyte has a sharply expressed anomalous character.
3. The curve of the temperature coefficient of electrical conductivity passes through a maximum at 50 mol. %, indicating the existence in the system of the compound $C_6H_5NH_2 \cdot SbCl_3$, whose presence is also reflected in the isotherms of electrical conductivity in a form which has been altered and complicated by a temperature minimum.
4. In the region of low antimony chloride concentrations, the course of the curve of the temperature coefficient of electrical conductivity is more complicated. This is probably due to the influence of unstable complex compounds formed in the system.

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THE ELECTRICAL CONDUCTIVITY AND VISCOSITY OF THE SYSTEM

ACETIC ACID - MONOCHLOROACETIC ACID. IV

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This system was studied by Kendall by the method of thermal analysis [1] and the method of electrical conductivity [2]. Having obtained a melting point diagram with a single eutectic, the author concluded that no complex compounds were formed in the system because of the small difference in the strength of the acids composing the system. However, from the melting point diagram given by Kendall, it is impossible to say with assurance that the components do not react chemically, as the melting points obtained are very widely separated. In addition, it is known that the melting point diagram does not always show the presence of chemical interaction observed by other methods [3]. The data obtained by Kendall for the electrical conductivity of the system are in contradiction with the conclusions drawn by him on the basis of thermal analysis.

The electrical conductivity curve, constructed by Kendall and Gross, along its entire length is convex to the axis of composition, and passes through a maximum at 25 mol. % $C_2H_4O_2$. The authors observe that the maximum values of the electrical conductivity may not correspond to the composition of the compound, as the electrical conductivity is affected by the viscosity, and a change in composition changes the complexity of the ions. The position of the maximum on the curve of electrical conductivity does not in general correspond to the composition of the compound, but the appearance of a maximum does show the presence of chemical interaction and the formation of a compound, [3].

The electrical conductivity of monochloroacetic acid, both in pure form and in aqueous solution greatly exceeds the electrical conductivity of acetic acid (pure and in aqueous solution), as is shown by our data as well as by the data of other authors [4]. The difference in strengths of these acids must be great enough so that upon mixing a chemical reaction will take place with the appearance of an acid-base relation.

Tartakovskaya, who studied the system $HNO_3 - CH_2ClCOOH$, arrived at the conclusion that there was no chemical reaction in the system, as both components were acids of approximately the same strength, and no acid-base relation was manifested when they were mixed. In a previous investigation, we showed that $C_2H_4O_2$ reacts chemically with HNO_3 , and that in view of the fact that $CH_2ClCOOH$ has almost the same strength as HNO_3 , the mixing of $C_2H_4O_2$ and $CH_2ClCOOH$ must result in reaction, for in the manifestation of an acid-base relation, the role of the acid can be fully played by the stronger (although only slightly) $CH_2ClCOOH$ [5].

It was of interest to investigate the reflection of the behavior of the system on the composition-property diagram, for the components were to a high degree stably associated, and upon mixing there could be a weakly expressed chemical reaction. With this purpose, we studied the electrical conductivity and the viscosity of the system $C_2H_4O_2 - CH_2ClCOOH$ at several temperatures.

The Electrical Conductivity of the System $C_2H_4O_2 - CH_2ClCOOH$

Monochloroacetic acid was first purified by fractional distillation (boiling point 139°), then recrystallized in sealed ampoules. Anhydrous $C_2H_5O_2$ was obtained in the same manner as in our preceding experiments. The electrical conductivity of this system could not be measured by the usual Kohlrausch method, because of the low conductivity of the system with all ratios of components; the measurements were therefore carried out in a set-up with a mirror galvanometer at 40° , 60° , and 75° . The electrical conductivity was calculated for a definite constant value of the current strength, the current passing through for 2 to 3 minutes.

The results of the measurement of the specific electrical conductivity are given in Table 1 and shown graphically in Fig. 1.

The character of the diagrams of specific electrical conductivity obtained by us is in full agreement with Kendall's diagram. As the temperature rises, the electrical conductivity increases. For all temperatures, the isotherms are convex to the axis of composition

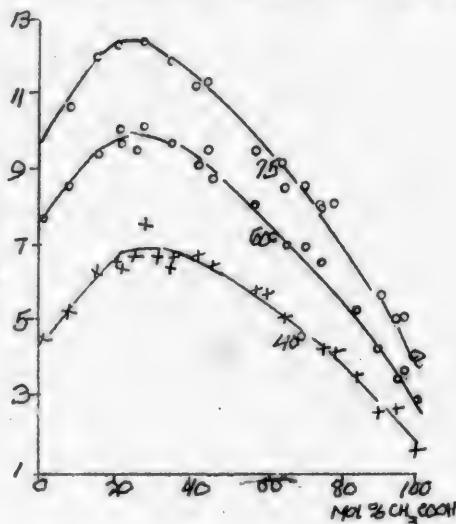


Fig. 1. Isotherm of electrical conductivity.

TABLE 1*

Mol. % $C_2H_4O_2$	Specific electrical conductivity			Mol. % $C_2H_4O_2$	Specific electrical conductivity		
	40°	60°	75°		40°	60°	75°
0	4.40	7.60	9.80	45.44	6.48	8.71	—
7.83	5.25	8.48	10.60	57.32	5.82	8.01	9.45
15.03	6.31	9.36	11.90	60.04	5.69	—	—
20.50	6.45	9.95	12.20	64.88	5.06	6.98	8.42
21.78	6.31	9.59	—	70.29	—	6.89	8.51
25.39	6.67	9.43	—	74.38	4.28	6.49	8.03
27.17	7.45	10.06	12.28	78.23	4.21	—	8.08
30.99	6.72	—	—	83.41	3.55	5.19	—
34.60	6.31	—	—	88.81	2.65	4.20	5.55
35.04	6.64	9.66	11.80	94.16	2.72	3.35	4.95
41.42	6.72	9.00	11.11	96.07	2.09	3.53	4.95
44.50	9.40	11.20	—	100	1.60	2.70	4.00

along their entire lengths, while the usual curves have one of their branches concave. There is a clearly expressed maximum on the isotherms, as with Kendall's curve, in the region of high monochloroacetic acid content, (25 mol. % $C_2H_4O_2$).

As the curves of specific electrical conductivity differ in form from the curves of the "ideal" systems studied by Usanovich, Tartakovskaya, and others [5], we may suppose that in this system a chemical reaction actually takes place.

For the temperature interval from 40 to 60° , the relative temperature coefficient of electrical conductivity was calculated (Table 2, Fig. 2).

The values of the electrical conductivity are given in arbitrary units.

TABLE 2

Mol. % $C_2H_4O_2$	Specific electrical conductivity		$C \cdot 10^{-2}$ 40-60
	40°	60°	
0	1.60	2.70	3.44
5	5.05	8.25	3.17
10	5.65	8.90	2.88
15	6.20	9.45	2.62
20	6.70	9.80	2.31
25	6.95	9.90	2.12
30	6.95	9.79	2.04
35	6.85	9.60	2.01
40	6.65	9.25	1.95
45	6.40	8.85	1.91
50	6.10	8.40	1.88
55	5.74	7.95	1.92
60	5.40	7.50	1.94
65	5.00	6.96	1.96
70	4.60	6.50	2.06
75	4.15	5.90	2.11
80	3.65	5.30	2.26
85	3.20	4.70	2.34
90	2.65	4.05	2.64
95	2.10	3.40	3.09
100	1.50	2.60	3.67

The curve for the temperature coefficient of electrical conductivity is concave along its entire length to the axis of composition and has a minimum at the equimolecular ratio of the components. Thus, we may assume that chemical reaction results in the formation of a compound of the composition $C_2H_4O_2 \cdot CH_2ClCOOH$, the value of whose temperature coefficient of electrical conductivity is less than that for the individual components of the system.

The molecular electrical conductivity has been calculated for $C_2H_4O_2$ and $CH_2ClCOOH$ as electrolytes (Table 4, Figs. 3 and 4).

The curve of molecular electrical conductivity for monochloroacetic acid as electrolyte (Fig. 3) is anomalous. At very low dilutions it rises sharply, then (after 200 μ) the slope becomes less steep, and upon further dilution, the curve becomes a straight line.

The curve of molecular electrical conductivity (Fig. 4) obtained on the basis of $C_2H_4O_2$ as electrolyte, is also anomalous. As the dilution is increased, it rises continuously along a curve slightly deviating from a straight line.

Consequently, the anomalous character of the curves of molecular electrical conductivity [10, 11] once more indicate that neither $C_2H_4O_2$ nor $CH_2ClCOOH$ are electro-

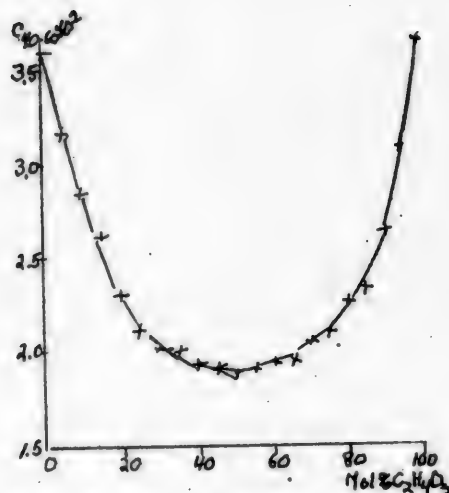
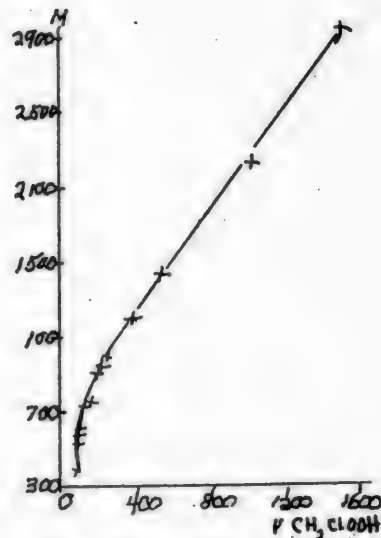


Fig. 2. Temperature coefficient of electrical conductivity

Fig. 3. Molecular electrical conductivity, calculated for $CH_2ClCOOH$ as electrolyte.

lytes in this system, and that the compound obtained apparently again undergoes electrolytic dissociation.

TABLE 3

Weight % $C_2H_4O_2$	$C_2H_4O_2$		$CH_2ClCOOH$	
	Dilution	Molecular electrical conductivity	Dilution	Molecular electrical conductivity
7.83	551.7	3227.0	73.80	431.7
9.76	449.0	2761.4	76.48	470.4
14.06	317.3	2126.0	81.74	547.7
19.15	237.9	1641.5	88.73	612.2
25.39	183.9	1259.7	98.55	651.1
15.03	298.1	2012.1	83.04	560.5
30.99	153.7	1014.4	108.60	716.75
34.60	139.4	885.2	116.10	737.20
45.93	100.9	560.0	134.90	748.7
54.55	94.41	476.80	178.40	900.9
60.04	87.35	397.44	206.70	940.5
64.84	82.18	345.20	238.60	1002.1
76.16	72.27	236.85	363.60	1200.0
83.44	66.15	182.57	524.90	1448.7
91.09	63.03	138.66	1015.00	2233.0
93.94	61.71	120.95	1503.00	2946.0

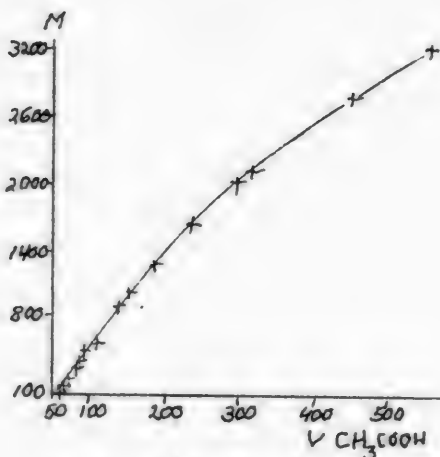


Fig. 4. Molecular electrical conductivity calculated for $C_2H_4O_2$ as electrolyte.

The Viscosity of the

System $C_2H_4O_2 - CH_2ClCOOH$

The viscosity (Table 4) was determined at the same temperatures as the electrical conductivity (40°, 60°, and 75°). The measurements were carried out by the method described in our previous work.

The results of the measurements are shown graphically in Fig. 5.

From this figure it can be seen that in the region of low concentration of $C_2H_4O_2$ (especially at 75°) the viscosity decreases slightly. With an increase in the content of acid, the decrease of viscosity is more noticeable, but not as sharp as that observed in ideal systems [5]. Thus the forms of the viscosity isotherms obtained by us differs from those of ideal systems,

and consequently, we may assume that the components here react chemically with each other.

The same type of diagram was obtained by Kurnakov [6] and later by Usanovich [7] and Terpugov [8] for systems in which compounds of low stability were formed. In addition, these S-shaped curves, as Usanovich calls them, were obtained for systems in which the viscosity of the compound formed was less than the viscosity of one of its components. Usanovich [7] observes that the points of inflection of

TABLE 4

Mol. % $C_2H_4O_2$	Viscosity $\eta \cdot 10^{-2}$			Mol. % $C_2H_4O_2$	Viscosity $\eta \cdot 10^{-2}$		
	40°	60°	75°		40°	60°	75°
0	3.807	2.375	1.636	47.08	2.413	1.512	1.221
9.06	3.787	2.276	1.630	50.28	2.051	1.447	1.108
10.25	-	-	1.548	57.44	1.723	1.264	1.057
13.36	3.627	2.210	1.543	65.87	1.604	1.104	0.916
18.03	3.548	2.200	1.530	74.59	1.436	1.008	0.799
26.68	-	1.958	1.500	76.10	1.409	0.987	0.758
31.07	2.807	1.774	1.432	83.71	1.159	0.806	0.699
37.02	2.763	1.792	1.405	92.08	0.994	0.762	0.608
44.71	2.432	1.617	1.284	100	0.870	0.630	0.536

the S-shaped curves play the same role as the maxima of the viscosity isotherms of irrational systems. On our curves, the point of inflection is displaced as the temperature rises, toward the less viscous $C_2H_4O_2$. It follows, therefore, that in agreement with what Usanovich has indicated, the coefficient of viscosity of the compound formed in the system is more than half the sum of the viscosity coefficients of the components, and its value is close to the viscosity coefficient of the more viscous $CH_2ClCOOH$.

TABLE 6

Mol. % $C_2H_4O_2$	$\Delta \eta$		
	40°	60°	75°
0	0.0007	0.0002	0.0001
10	0.0030	0.0013	0.0005
20	0.0042	0.0022	0.0008
30	0.0043	0.0024	0.0013
40	0.0042	0.0023	0.0019
50	0.0038	0.0021	0.0017
60	0.0029	0.0020	0.0014
70	0.0024	0.0017	0.0011
80	0.0020	0.0010	0.0009
90	0.0014	0.0007	0.0006
100			

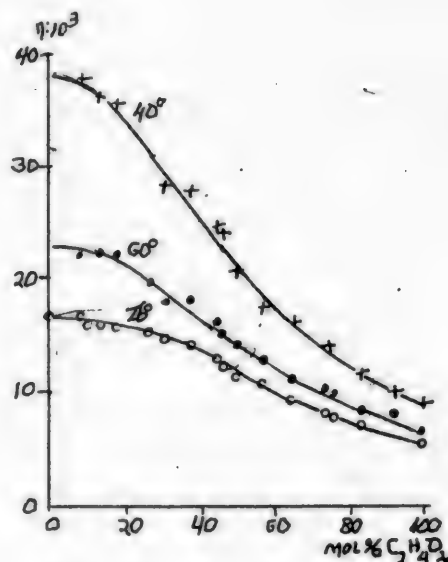


Fig. 5. Viscosity isotherms

Usanovich observes also that if we carry out a graphic differentiation of the viscosity curves, then the maximum produced on them is displaced, as the temperature is lowered, to the ordinate of the compound formed in the system.

The diagrams obtained by us by graphic differentiation of our viscosity curves (Table 6) are given in Fig. 6.

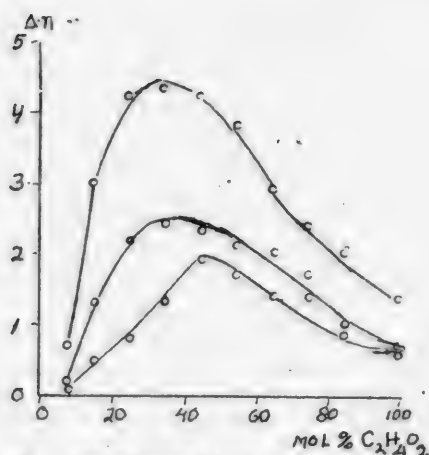


Fig. 6. Differential viscosity curves.

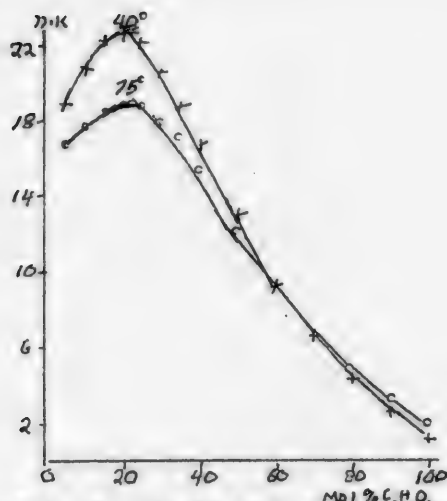


Fig. 7. Isotherms for corrected Electrical Conductivity.

A comparison of these diagrams with the two possible diagrams given by Usanovich shows that it resembles the diagram of Fig. 3, with only this difference, that the maxima of our diagram are situated completely on the other side.

Upon lowering the temperature, therefore, the maxima, in contradiction to those on Usanovich's diagram, are displaced further away from the ordinate representing the composition of the compound formed.

In order to determine the change of electrical conductivity with the concentration independently of the viscosity, the influence of the latter was eliminated (Table 5) and curves were constructed for the "reduced" conductivity (Fig. 7).

It is clear from the figure that the viscosity has a considerable influence on the electrical conductivity. The elimination of this influence results in

TABLE 5

Mol. % $C_2H_4O_2$	40°			60°			75°		
	κ	$\eta \cdot 10^{-2}$	$\kappa \cdot \eta \cdot 10^{-2}$	κ	$\eta \cdot 10^{-2}$	$\kappa \cdot \eta \cdot 10^{-2}$	κ	$\eta \cdot 10^{-2}$	$\kappa \cdot \eta \cdot 10^{-2}$
5	5.05	3.77	19.00	8.25	2.25	18.56	10.40	1.61	16.74
10	5.65	3.70	20.90	8.90	2.23	19.85	11.15	1.60	17.84
15	6.20	3.59	22.26	9.45	2.19	20.70	11.80	1.58	18.64
20	6.70	3.40	22.78	9.80	2.10	20.58	12.25	1.55	18.99
25	6.95	3.18	22.10	9.90	2.00	19.80	12.40	1.53	18.97
30	6.95	2.98	20.81	9.85	1.88	18.52	12.25	1.47	18.01
35	6.85	2.75	18.84	9.60	1.74	16.70	11.95	1.43	17.09
40	6.65	2.55	16.96	9.30	1.64	15.25	11.55	1.34	15.48
50	6.10	2.13	12.99	8.45	1.41	11.91	10.65	1.15	12.25
60	5.40	1.75	9.45	7.50	1.20	9.00	9.59	0.98	9.40
70	4.60	1.46	6.72	6.50	1.00	6.50	8.40	0.84	7.06
80	3.65	1.22	4.45	5.30	0.83	4.40	7.10	0.70	5.00
90	2.65	1.02	2.70	4.05	0.73	2.96	5.50	0.61	3.35
100	1.50	0.88	1.32	2.70	0.66	1.78	3.90	0.55	2.14

a change of the right branch of the curve of electrical conductivity from concave to the axis of composition to convex; during this process, the isotherms acquire the form usually observed for them. The figure shows also that upon "correction" of the electrical conductivity, there is also a considerable change in the values of the electrical conductivity.

SUMMARY

1. A study has been made of the electrical conductivity of the system $C_2H_4O_2 - CH_2ClCOOH$ at 40°, 60°, and 75°.
2. The temperature coefficient of electrical conductivity has been calculated for the interval 40-60°. The minimum value occurs at 50 mol. %, which permits us to assume the formation in the system of a compound with the composition $C_2H_4O_2 \cdot CH_2ClCOOH$. As the electrolytic dissociation of the complex changes to a lesser degree with the temperature (minimum on the diagram) we may suppose that its stability is greater than the stability of the components of the system.
3. The maximum on the isotherms of electrical conductivity indicates a certain increase in the electrical conductivity of the newly formed compound with a greater tendency to salt formation; as this has a somewhat greater stability, it undergoes thermal dissociation to a lesser degree and is dissociated to a greater degree into ions, apparently being the electrolyte of the system.
4. If the compound has the composition $C_2H_4O_2 \cdot CH_2ClCOOH$, its properties will differ little from the properties of the individual components of the system, and therefore its presence will not find any high degree of reflection in such diagrams as those of viscosity or melting point.
5. The viscosity of the system has been investigated at 40°, 60°, and 75°. S-shaped curves are obtained, indicating that the value of the viscosity of the newly formed compound is intermediate between the values of the viscosities of the components.
6. The viscosity curves have been differentiated graphically. The curves obtained show a displacement of the maximum (when the temperature is lowered) from the ordinate of the compound formed in the direction of $CH_2ClCOOH$. It is possible that this displacement [7] is determined by the presence in the system at low temperatures of a large quantity of the dimer of monochloroacetic acid.
7. Upon eliminating the influence of the viscosity upon the electrical conductivity, the isotherms of the latter assume the usual forms observed (one branch concave, the other branch convex to the axis of composition); when both branches are "uncorrected" they are both convex to the axis of composition. The latter fact may possibly be explained by the lowered rate of decrease of the viscosity (upon dilution) as a result of the presence of associated molecules.
8. The curves of the "reduced" electrical conductivity show that with an increase in temperature, the electrical conductivity of both pure $CH_2ClCOOH$, as well as of solutions with a high content of this substance decreases, while the electrical conductivity of $C_2H_4O_2$ and its solutions increases. This, in all probability, is the result of the influence on the electrical conductivity of the system of the electrical conductivity of the individual components. The decrease in electrical conductivity in one part of the diagram may be the result of a decrease in the number of associated (ion-forming) molecules of $(CH_2ClCOOH)_2$. The increase in conductivity in the other part is due, apparently, to the greater electrolytic dissociation of the dimer $(C_2H_4O_2)_2$ in comparison with thermal dissociation. It is possible that if the individual conductivity of each of the acids is calculated from the over-all value of the conductivity of the system, then with a change in composition, the electrical conductivity will change chiefly because of the electrical conductivity of the compound formed, and there will be

a maximum at the composition of the compound formed.

9. Thus, the results of an investigation of the system $C_2H_4O_2 - CH_2ClCOOH$ indicate a fairly great influence of the process of dissociation of the polymerized molecules upon the behavior of the system during a change in its composition. As a result of the weakly expressed chemical reaction between components which differ little in acid strength, this process, apparently, takes place to an insufficient degree, and the dimers of the acids present result in a certain degree of deviation from the standard forms of composition-property diagrams.

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THE SULFATES OF TETRAVALENT TITANIUM

XIX. THE CHEMISTRY OF TITANIUM [1]

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In Hoffman's [2] lexicon of inorganic compounds, he lists nine sulfates of tetravalent titanium, most of them in the form of hydrates of the normal sulfate, or basic, so-called titanyl sulfates.

Thus, according to Glätzl, [3] upon treating the sulfate of tetravalent titanium with nitric acid, a titanium sulfate is formed with the composition $\text{Ti}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$, as a transparent tarry mass. Faber [4] obtained the sulfate in the molecular ratio $\text{TiO}_2:\text{SO}_3 = 1:2.2$, which corresponded to the normal sulfate of titanium with a small excess of sulfuric acid. Ramsay and Usher [5] in their investigation of the action of radium emanation on aqueous solutions of salts, used, according to their data, an aqueous solution of $\text{Ti}(\text{SO}_4)_2$. Merz [6], by evaporating a solution of titanic acid in sulfuric, obtained a sulfate with the composition TiOSO_4 . According to Blondell [7], who is quoted in the literature most often of all, this salt and sulfates of the composition $-\text{TiO}_2 \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$; $2\text{TiO}_2 \cdot 3\text{SO}_3 \cdot 3\text{H}_2\text{O}$; $2\text{TiO}_2 \cdot \text{SO}_3 \cdot \text{aq}$; $7\text{TiO}_2 \cdot 2\text{SO}_3 \cdot \text{aq}$ - crystallize from hot sulfuric acid solutions, but from dilute solutions kept for a long time at room temperature, a sulfate of the composition $5\text{TiO}_2 \cdot \text{SO}_3 \cdot 5\text{H}_2\text{O}$ separates out. The work of this author lists no experimental data confirming the formulas listed above. Rosenheim and Schütte [8] also obtained, from alcoholic solutions of sulfuric acid with the hydrate of titanium oxide, a monosulfate of the composition $\text{TiOSO}_4 \cdot 5\text{H}_2\text{O}$. Lothar Wöhler, Pluddemann, and Wöhler [9] obtained a basic sulfate with the composition $\text{TiO}_2 \cdot \text{SO}_3$ and determined its vapor pressure curve. A product decomposing into the basic sulfate $2\text{TiO}_2 \cdot \text{SO}_3$ gave a different, lower vapor pressure curve, which was identical with the curve of the product of decomposition of $\text{TiO}_2 \cdot \text{SO}_3$.

The authors assert that their data contradict the data of Faber and others with regard to the preparation of a series of titanyl sulfates. Thus, they could not obtain an anhydride of higher sulfate content than corresponded to the formula $\text{TiO}_2 \cdot \text{SO}_3$. There have been indications of the formation of other basic sulfates. Wöhler and Faber, for example, indicate the existence of a salt of the composition $3\text{TiO}_2 \cdot \text{SO}_3$.

American authors [10] prepared a basic sulfate of titanium starting with titanium tetrachloride or commercial titanium sulfate containing 5.36% more SO_3 than corresponded stoichiometrically to $\text{Ti}(\text{SO}_4)_2$. There are also indications with regard to a commercial product of this composition in the monograph by Thornton [11]. Zborovsky and Germogenova [12] describe a monosulfate, $\text{TiO}_2 \cdot \text{SO}_3$, which separated after long standing from the solution obtained by evaporating sulfuric acid solutions of titanium.

The articles of Boguslavskaya [13] contain more information on this question than do any others. According to her data, sulfuric acid solutions obtained by dissolving hydrated titanium dioxide in an excess of sulfuric acid give a dihydrate of titanium sulfate from the hot solutions upon concentration of the

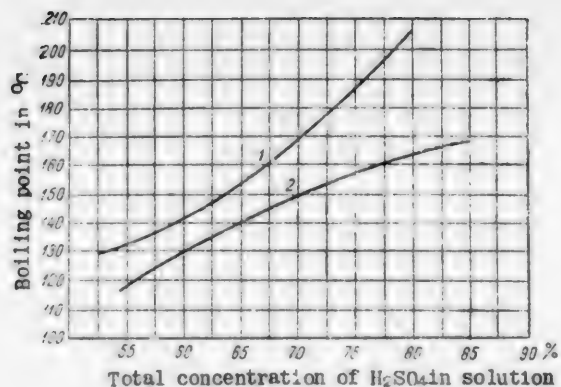


Fig. 1 Boiling point of sulfuric acid solutions of titanium dioxide with the ratio $\frac{H_2SO_4}{TiO_2} = 4:3$

1-boiling points of sulfuric acid;
2-boiling points of sulfuric acid solutions of titanium dioxide



Fig. 2

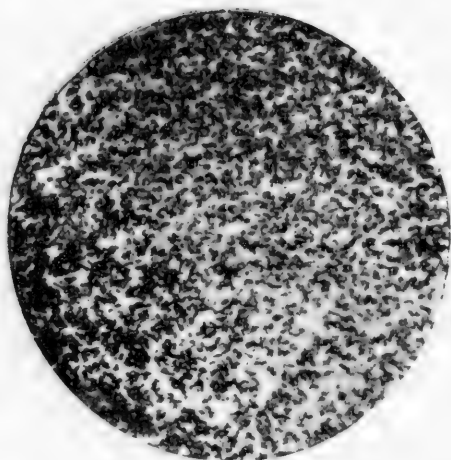


Fig. 3

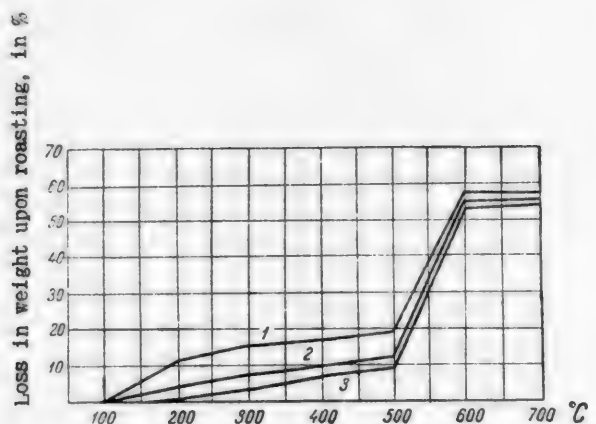


Fig. 4 Decomposition of Sulfates upon Heating

1-Obtained at concentration of H₂SO₄ in solution of 63.4%; 2-obtained at concentration of H₂SO₄ in solution of 71.4%; 3-Obtained at concentration of H₂SO₄ in solution of 83.6%.

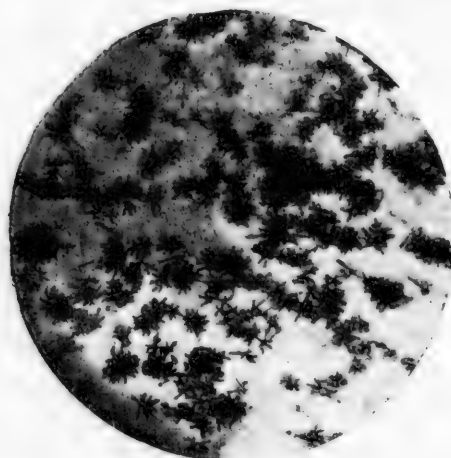


Fig. 5

sulfuric acid from 50 to 90%. The tetrahydrate of the normal sulfate of titanium separated only upon the decomposition of potassium fluorotitanate with sulfuric acid.

There are essential inaccuracies in Boguslavskaya's statement. Thus, the data on temperature and concentrations of acid in a number of cases do not correspond to the facts. In particular, the crystallization temperatures indicated are the boiling points of solutions of sulfuric acid at the corresponding concentrations. Apparently, in the process of heating, as a result of evaporation, the concentration of acid is considerably changed, so that the data on concentration refer to the initial period, and not to the moment of crystallization. In a later article, describing a "new method" for obtaining titanyl sulfate, the novelty consists in lowering the concentration of sulfuric acid used for purposes of solution to 50-60%. However, if we recalculate the data listed in a table of the first of these articles, then there is a 50% concentration of acid only in the second experiment, while in all the rest the concentration is above 60%. Thus, this article gives nothing new in comparison with the first. The author indicates that for solution she also used the commercial metatitanic acid. The complicated mixture usually called metatitanic acid is a hydrated titanium dioxide containing sulfate ion; it is insoluble in aqueous solutions of sulfuric acid. It can be brought into solution by treatment corresponding to the factory operations for the decomposition of the original raw material. Only freshly formed precipitates dissolve in acid.

Similar reports are encountered in the literature, and we have confirmed a large number by systematic observations on the solubility of preparations which had been precipitated different lengths of time previously.

The work of Boguslavskaya does not permit us to determine the conditions of crystallization of titanium sulfate insofar as they depend on the concentration of sulfuric acid.

Preparation of Solutions

To obtain the sulfates, we started with the commercial metatitanic acid characterized in Table 1.

TABLE 1

Characteristics of the Original Preparations of Metatitanic Acid

No. of expt.	Specimen	Composition product dried at 110°, in %				Moisture at 110° (%)	Fineness of mesh (open- ings per sq cm)
		TiO ₂	SO ₃	H ₂ O	Total		
1	Air-dried	72.78	7.31	19.68	99.77	6.68	10.000
2	Air-dried	74.81	6.92	18.12	99.85	8.50	10.000
3	Covered with unpressed solution (before fil- ter press)	85.55	5.21	9.05	99.81	27.0-42.0 (prelim- inary drying with filter paper)	-

Because of the insolubility mentioned above, freshly precipitated preparations were prepared by treating the original product with 60-80% sulfuric acid by the usual method ("decomposition") [14], followed by lixiviation and separation under the conditions of Mecklenburg ("hydrolysis") [15]. These samples, dried at 110°, contained from 62 to 80% of titanium dioxide, and 27-45% moisture. Before solution, they were kept for from 3 to 10 days. These preparations dis-

dissolved completely in sulfuric acid of a concentration not below 60%. As an illustration of its solubility, which decreased in the course of time, Table 2 can serve.

TABLE 2
Solubility of Metatitanic Acid

No. of Expt.	Amount of moist metatitanic acid (in g.)	Moisture in metatitanic acid (in %)	TiO ₂ content in dry metatitanic acid (in %)	Amount of H ₂ O ₂ (1-84) (in ml.)	Amount of water (in ml.)	Concentration of H ₂ SO ₄ in ext.	Temperature of solution (in °)	Time for complete solution (in min.)	RESULTS
1	41.6	31.5	64.6	43.5	78.6	46.6	95-100	-	did not dissolve completely
2	39.9	33.6	79.9	49.2	60.3	55.1	118	-	"
3	24.7	28.3	72.9	31.0	38.0	56.0	120	-	"
4	10.0	37.3	75.7	11.0	8.9	60.8	132	-	dissolved completely
5	17.5	39.2	79.8	20.2	15.8	61.0	130	-	"
6	43.8	35.0	79.7	54.0	42.6	63.2	140	60	"
7	50.0	29.1	62.0	51.7	40.8	63.4	138	60	"
8	42.4	31.4	70.0	48.6	38.3	63.4	139	65	"
9	15.0	39.2	79.8	18.5	10.7	66.0	143	60	"
10	54.2	28.2	80.0	73.0	45.7	68.9	148	40	"
11	10.0	37.3	75.0	11.0	5.0	69.6	149	40	"
12	12.0	35.7	77.8	15.3	4.2	70.6	153	40	"
13	14.0	19.7	74.7	20.1	9.0	74.3	155	35	"
14	26.0	40.5	69.2	25.6	11.8	76.0	157	-	"
15	11.4	37.3	75.0	12.6	2.6	77.3	159	-	"
16	12.0	33.7	77.8	15.3	-	80.0	167	-	"
17	14.7	19.7	74.7	20.6	4.2	82.6	165	-	"
18	10.0	37.3	75.0	11.0	-	85.0	169	-	"

These experiments (Table 2) were carried out at constant concentration with a reflux condenser and a stirrer with a mercury seal, and an excess of acid, equal to 4.3. This excess was close to the minimum necessary for complete solution; as determined for concentrations of acid from 60-70%, it was equal to four. According to the data of Table 2, a concentration of acid not below 60% was necessary for complete solution.

A comparison of the boiling points of solutions and of pure sulfuric acid of the same concentration is given graphically in Fig. 1. It shows that in concentrated solutions a greater combination with the sulfuric acid is observed, as shown by a much lower boiling point of the solutions. This is probably due to the formation of complexes, whose presence in sulfuric acid solutions of titanium has been assumed by a number of authors [10].

The Crystallization of Titanium Sulfates

If we start with normal titanium sulfate, $Ti(SO_4)_2$, then the ratio of sulfuric acid and titanium dioxide must equal 2.45; for the formation of basic titanium sulfate, $TiOSO_4$, it equals 1.23. Crystallization was carried out from solutions with ratios varying from 1.5 to 8, during heating to the boiling point in round-

In experiment 1 the process of solution was carried out on the water bath at a temperature of 95-100°.

** In experiments Nos. 12 and 16, H₂SO₄ was used of sp. gr. 1.83, 92% concentration.

TABLE 3

Crystallization of Titanium Sulfate with Different Concentrations of Sulfuric Acid in Solution

No of solution corresponding to Table 2	Conc. H_2SO_4 in solution of metatitanic acid in %	Time of crystallization, hours	Percent yield of $TiO(2SO_4)_2 \cdot H_2O$ based on TiO_2	Form of precipitate under microscope	
				At time of crystallization	After crystallization
2	55.1	11.1	91.9	needles of titanyl sulfate and metatitanic acid	Needles of titanyl sulfate and metatitanic acid
3	56.0	10.7	93.0	Same	Same
4	60.8	12.0	94.3	needles of titanyl sulfate	needles of titanyl sulfate
5	61.0	12.0	—	Same	Same
6	63.2	12.2	—	"	"
7	63.4	12.0	96.2	"	"
8	63.4	11.8	95.1	"	"
9	66.0	12.2	96.1	"	"
10	68.9	13.2	94.0	"	"
11	69.6	13.3	—	needles of titanyl sulfate plus powdery precipitate	needles of titanyl sulfate plus powdery precipitate
12	70.6	13.5	—	Same	Same
13	74.3	14.0	—	"	"
14	76.0	13.3	—	powdery precipitate	powdery precipitate
15	77.3	14.7	—	Same	Same
16	80.0	15.0	—	"	"
17	82.6	15.5	—	"	"
18	85.0	15.6	—	"	"

bottomed flasks fitted with reflux condensers for a period of 3 to 8 hours. In isolated instances, a voluminous precipitate formed quickly. Sometimes the metatitanic acid did not dissolve completely, and then crystallization began from the cloudy solutions. The precipitates formed were examined under the microscope. They were suctioned dry on the Buchner funnel and washed with alcohol until there was a negative reaction for sulfate. They were analyzed after drying at 110° .

The conditions of crystallization, and the character of the precipitates obtained in relation to the concentration of sulfuric acid in the solution at one and the same ratio $\text{H}_2\text{SO}_4:\text{TiO}_2 = 4:3$, are given in Table 3.

The precipitates obtained at different concentrations of sulfuric acid differed sharply in their microcrystalline structure. As was shown by the analyses, listed in Table 4, upon solution of metatitanic acid in 60-70% sulfuric acid, pure titanyl sulfate crystallizes out in the form of long needles (microphotograph, Fig. 2).

TABLE 4
Chemical Composition of Titanyl Sulfate

Sample No.	1	2	3	4	5	6	$\text{TiO}_2 \cdot \text{SO}_4 \cdot 2\text{H}_2\text{O}$ theoretical composition
Temperature of crystallization Content (in %)	132	140	138	138	148	148	-
TiO_2	42.10	42.52	42.73	43.15	42.81	42.67	40.79
SO_3	39.71	39.32	40.20	43.13	39.66	39.58	40.83
H_2O by difference from loss of weight upon roasting.....	18.39	18.44	17.20	14.48	17.31	17.85	18.38
Total.....	100.20	100.28	99.83	100.76	99.78	100.10	100.0
Loss of weight upon roasting (800°)	58.10	57.56	57.40	57.60	56.97	57.43	59.21

Upon dissolving metatitanic acid in 56-60% sulfuric acid there is obtained a titanyl sulfate contaminated by an admixture of insoluble metatitanic acid. With a higher concentration of sulfuric acid in solution, more than 70% of the precipitate obtained by crystallization has an essentially different form under the microscope. The needles of titanyl sulfate are sharply differentiated from the round granules of this compound (microphotograph, Fig. 3).

TABLE 5
Analysis of the precipitates from concentrated solutions

No. of Exp.	Conc. of H_2SO_4 during solution of metatitanic acid, taking accounting of moi- sture in the meta acid (%)	Acid factor $F = \frac{\text{H}_2\text{SO}_4}{\text{TiO}_2}$	Time of crystal- lization (hours)	Temper- ature of cry- stalliz- ation (in °C)	Composition of precipitate		
					TiO_2 (%)	SO_3 (%)	H_2O % (by dif- ference)
1	69.2	4.6	4	143	44.35	40.66	14.99
2	71.4	4.6	4.5	153	44.50	42.14	13.36
3	74.3	4.3	5.5	155	43.91	42.28	13.81
4	82.6	4.3	4.5	165	44.91	42.52	12.57
5	83.6	4.6	4	178	45.53	45.06	9.51

In individual cases with a concentration of sulfuric acid from 70 to 76%, the precipitates are mixtures of titanyl sulfate and these products. The analysis of these compounds, which do not contain apparent admixtures of needles is given in Table 5; it shows that the ratio of TiO_2 to SO_3 in these precipitates is close to 1:1.

The precipitates of titanyl sulfate in the form of needles, which had been washed with alcohol and dried at 80° , as well as those precipitates which had separated from solutions with a concentration of sulfuric acid above 70%, did not dissolve completely in cold and hot water. They dissolved completely upon standing in the cold in 0.5-1% sulfuric acid solution.

The manner of decomposition of the precipitates upon heating is given in Table 6 and in Fig. 4.

TABLE 6
Decomposition of sulfates upon heating

No. of exp.	Conc. H_2SO_4 during solution of metatitanic acid (in %)	Composition of precipitate (%)					Loss upon roasting						
		TiO_2	SO_3	H_2O	total	loss upon roasting	200°	300°	400°	500°	600°	700°	Total
1	63.4	42.40	40.20	17.80	99.83	57.96	11.16	4.11	1.06	2.23	38.83	-	57.44
2	71.4	44.50	42.14	13.36	100.0	55.50	4.64	3.21	2.12	1.92	42.90	0.81	55.60
3	83.6	45.55	45.06	9.51	100.0	54.57	0.25	3.69	3.65	1.81	43.76	1.02	54.20

Sulfur trioxide was evolved in the temperature interval $500-600^\circ$; this is in accord with the data of Wohler and Plüddemann, who investigated the vapor pressure curve of anhydrous titanyl sulfate.

Taking into account the fact that the most convenient concentration of sulfuric acid for the preparation of pure titanyl sulfate is from 50 to 70%, we determined the possibility of crystallization of the titanyl sulfate in relation to the ratio of sulfuric acid to titanium dioxide between the limits 1.5 to 8.

From the data of Table 7 it is clear that the pure dehydrated titanyl sulfate in the form of needles can be obtained at a ratio of from 3 to 7. At a ratio of 3, crystallization does not begin from a transparent solution; instead apparently, the small amount of remaining undissolved metatitanic acid dissolves as the crystallization of the titanyl sulfate proceeds, as in the crystals obtained no metatitanic acid is observed under the microscope.

An increase in concentration of sulfuric acid makes the crystallization of titanyl sulfate more difficult, as with an acid factor F equal to 7 and 8, a powdery precipitate is observed at the time of crystallization; this is then transformed completely, with F equal to 7, and incompletely, with F equal to 8, into needles.

We also investigated the possibility that titanyl sulfate might crystallize as a result of the decomposition of metatitanic acid with a small excess of sulfuric acid, equal to 1.5, with different concentrations of sulfuric acid.

For the decomposition, we took air-dried commercial metatitanic acid (sample No. 2, Table 1), and sulfuric acid from 60 to 90% concentration. The decomposition was carried out in porcelain dishes with stirring, and heating on the oil bath at a temperature from 110 to 155° . Both during the decomposition and afterwards, the reaction mixture was examined under the microscope. The data obtained are listed in Table 8.

TABLE 7

Crystallization of Titanium Sulfates at Different Concentrations

No. of expt.	Conc. of H_2SO_4 during solution of metatitanic acid (in %)	Acid factor $F = \frac{H_2SO_4}{TiO_2}$	Time of crystallization in hours	Temp. of crystallization °C	Form of precipitate under the microscope	
					At time of crystallization	After crystallization
1	61	8	7	134	Powdery precipitate	Needles of titanyl sulfate plus powdery precip.
2	61	7	8	127	Few crystals of titanyl sulfate plus powdery precipitate	Needles of titanyl sulfate
3	61	6	6	131	Needles of titanyl sulfate	Needles of titanyl sulfate
4	68	5	6	143	Same	Same
5	65	4	4	135	"	"
6	64	3	3	127	Needles of titanyl sulfate plus metatitanic acid	"
7	70	3	6	135	Same	"
8	60	2	2	124	"	Needles of titanyl sulfate plus metatitanic acid
9	70	1.5	2	124	"	Same
10	68	1.5	35	120	"	"

A study of the composition of the reaction mixture permitted us to draw the following conclusions. In the decomposition of commercial air-dried metatitanic acid by sulfuric acid, with F equal to 1.5, there take place in the reaction mixtures processes similar to those that take place during the decomposition of freshly precipitated metatitanic acid with a greater acid factor, F equal to 4.3

In the decomposition of metatitanic acid with sulfuric acid of 60, 70, and 85% concentration, the corresponding percentages of decomposition are 42, 84, and 75. It follows, therefore, that the most complete decomposition takes place with the 70% sulfuric acid, when needles of titanyl sulfate crystallize in the reaction mixture.

The decomposition of metatitanic acid by sulfuric acid of a concentration above 70% can also lead to the formation of titanyl sulfate in the form of needles; for this purpose, however the introduction of earlier prepared titanyl sulfate in the form of 'seeds' is necessary. Thus, if at the beginning of the decomposition

TABLE 8

Forms of crystallization of precipitates

No. of Expt.	Amount of metatitanic acid (in g)	Acid factor $\frac{H_2SO_4}{Fe_2O_3 \cdot TiO_2}$	Conc. H_2SO_4 in %	Time of decomp. (in hrs.)	Temp. of decomp. (in °)	Composition of reaction mixture after decomposition
1	30	1.5	60	1	110-140	Needles of titanyl sulfate plus powdery precipitate.
2	30	1.5	70	1	120-140	Same
3	30	1.5	70	2	110-150	Almost pure needles of titanyl sulfate
4	50	1.5	70	2.5	100-135	Same
5	30	1.5	80	1	135-150	Powdery precipitate
6	30	1.5	90	1	140-155	Same

titanyl sulfate amounting to 1% of the weight of metatitanic acid is added, a rapid crystallization of titanyl sulfate needles will take place in the mixture.

If the powdery precipitate separated from solutions of sulfuric acid with a concentration above 70% is kept in closed vessels, their form does not change. If, however, these precipitates and their solutions are exposed to the air, then, as a result of the absorption of moisture, the concentration of sulfuric acid in the solution diminishes, and the grains of the precipitate are transformed into needles of titanyl sulfate in the form of stars (microphotograph, Fig. 5).

The same process takes place in the decomposition of the titanomagnetite concentrate, as far as the structure of the products formed is concerned; this concentrate is the usual raw material for the preparation of titanium dioxide.

The peculiarities of the system titanium dioxide - sulfuric acid are shown in the fact that the conditions for the crystallization of titanium sulfate are not quite simple. Sometimes crystallization is considerably retarded; in certain cases, it does not fully take place.

In our laboratory work, we found one case where lengthy attempts to reproduce the conditions of crystallization described by Boguslavskaya did not result in the formation of a precipitate. Even after a long time it could not be obtained. Then with almost unchanged working conditions precipitates always began to form. The cause, apparently, was not the introduction from without of seed crystals, obtained to some extent from the precipitates produced in another laboratory, but a slight increase in the time of heating. The slowness of the attainment of an equilibrium condition, and the irreversibility of the system result in difficulties in applying the composition - properties diagram to a study of the composition of the products obtained; we therefore have reservations about citing the data of Sagawa [16], who determined in the system titanium dioxide - water - sulfuric acid at 100° and 150°, thirteen definite compounds, of which many had not previously been described in the literature. Lachinsky [17] cites these data, which do not show the temperatures at which these compounds were obtained by the author indicated.

SUMMARY

1. Of the sulfates of tetravalent titanium described in the literature, only the existence of the basic sulfate with the composition $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ can be considered definitely determined. We did not succeed in obtaining titanium sulfates with a ratio of SO_3 to TiO_2 greater than 1:1.

2. Pure titanyl sulfate in the form of needles crystallizes from solutions of freshly precipitated metatitanic acid in 60-70% sulfuric acid when the ratio of H_2SO_4 : TiO_2 is not less than 3 to 4. A higher concentration of sulfuric acid leads to the formation of precipitates with a lower water content.

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THE CRYSTALLINE MODIFICATIONS OF PLUMBIC FLUORIDE

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It is known from the literature that plumbic fluoride has two crystalline modifications, the cubic and the rhombic. These modifications have been investigated by Kolderup [1], by Ketelaar [2], and by Schumann [3]. In their investigations, these authors used plumbic fluoride obtained in the form of a powder, precipitated from lead nitrate and ammonium fluoride, or by dissolving lead carbonate in hydrofluoric acid. As is evident from the articles, both methods gave the rhombic modification. The cubic modification was obtained by roasting the rhombic. In these articles, however, there is much that is unclear and contradictory. The authors had considerable difficulty in the investigation because of the fact that the very small solubility did not permit them to obtain plumbic fluoride in the form of separate fairly large crystals. The object of our work was to obtain the modifications of plumbic fluoride in the form of larger crystals, and, using them, to study the properties of the modifications.

The reasons why it is impossible to obtain the difficultly soluble substance during the reaction in the form of larger crystals is partly that because of its small solubility it is impossible to limit the number of centers of crystallization formed. More and more centers of crystallization are formed, and this results in the separation of the substance in the form of microscopic crystals. Therefore, in order to obtain the substance in the form of large crystals, it is necessary that formation proceed very slowly, i.e., that the compound formed separate on a small number of centers of crystallization. Starting with this in mind, lead fluoride was obtained by the usual reaction of precipitation between lead and fluoride ions, but only when the reaction was carried out slowly, with the aid of diffusion.

This was accomplished in practice in the following manner: in a beaker of approximately 600 to 2000 ml capacity, there was placed another much smaller beaker (100 to 600 ml), and both were filled beyond the half-way mark with distilled water. Then, by means of a pipette, there was placed in the inner flask a definite amount of plumbic nitrate solution, and in the outer flask, a solution of ammonium fluoride. During this process, the solutions were let out of the pipette in such a way as to spread out over the bottom of the vessel. Equivalent amounts of the substances were placed in both beakers. Both beakers were then carefully filled with distilled water so that the liquids in them were joined, and in addition, more was added until a layer of approximately 4 to 6 cm covered the inner flask. The concentrations of lead nitrate and ammonium fluoride solutions, calculated for the entire filled outer beaker, ranged in these experiments from 0.5 N to 0.06 N. After the beaker was filled with water, it was covered with a watch glass, in order that the water might not evaporate upon prolonged standing, and it was allowed to stand in a place that was free from vibration. In order to protect the glassware from the action of the fluorine compound, the walls were coated with paraffin.

Only a few days after the beakers had been filled with water, the first micro-

scopic crystals had already made their appearance. After 2 or 3 months, depending upon the amount of materials taken, the growth of the crystals had usually been completed.

The method of cultivating crystals by means of diffusion has been previously utilized in several other cases. In this way, for example, crystals of lead sulfate have been obtained.

The method is especially suitable in those cases where the reaction gives a combination either of several modifications of one and the same compound or several compounds of different composition. If the reaction is carried out in these cases in the usual manner, it is impossible to determine any difference in the crystals obtained, as they are so tiny that their separation is impossible even under the microscope. Thus, this method of carrying out the reaction, in addition to giving the desired larger crystals, can also be utilized for the determination of the products of the reaction.

The crystals obtained by the method described above had dimensions up to 3 mm. Upon investigation under the microscope, it was found that both in external form and in fundamental properties they were very different. The greater part, like the usual crystals, were characterized by their luster and brittleness. These crystals had two forms - octahedra, and hexagonal plates. The rest of the crystals obtained were also hexagonal plates, but were **very** fine and soft. These plates could be easily bent or pierced with a small needle, without disintegrating as crystals ordinarily would. In size they were several times as large as the remaining crystals. Frequently, the crystals were opaque and had a granular structure.

Chemical analysis under the microscope of selected crystals of the first group showed that these were crystals of lead fluoride. Upon comparing the network constants (determined from the spacing of the layer lines of the roentgenograms of single crystals) with the data in the literature, it appeared that the octahedra were the cubic modification, and the shining hexagonal plates the rhombic modification of plumbic fluoride.

An investigation of the crystals obtained showed that the cubic modification always had only one form, that of octahedra (Fig. 1). The crystals of the rhombic modification had different forms. Those most frequently encountered are shown in Fig. 2.

The crystals of the rhombic modification were measured with a two-ring goniometer. In all, 9 crystals were measured. The averages for a number of measurements are given in Table 1.

The errors with which the coordinates of the different faces were measured varied. In separate measurements, they fluctuated between $\pm 0.1^\circ$ - 11° .

The results of our measurements showed that the crystals of the rhombic modification of plumbic fluoride could be referred to the class of rhombic dipyrramids.

The habits of the crystals of the rhombic modification were of different kinds. They changed depending both on the concentration of the solutions used for growth,

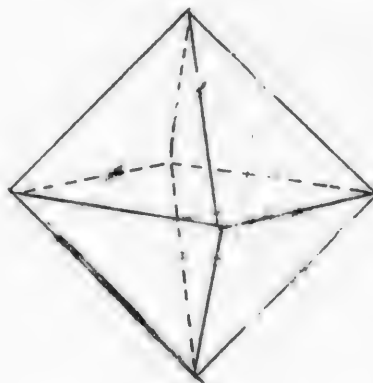


Fig. 1. Crystals of the cubic modification of plumbic fluoride.

TABLE 1

Symbol	Designation	Measured		Calculated	
		ϕ	ρ	ϕ	ρ
010	b	0°00'	90°02'	0°00'	90°00'
001	c	0 00	0 00	0 00	90 00
012	k	0 00	30 14	0 00	30 43
011	d	0 00	49 57	0 00	49 55
111	p	38 49	66 27	38 49	66 27
101	e	90 00	62 53	90 00	63 00
$a:b:c = 0.6094:1:1.1882$					

and on the starting materials (lead acetate or nitrate). The crystals most often encountered are sketched in Fig. 2-a. It is clear from that figure that the shape of these crystals is characterized by a strongly developed third pinacoid c [001]. Fig. 2-b depicts another type of crystal, which is characterized by a strongly developed second pinacoid b [010]. In addition to crystals of these

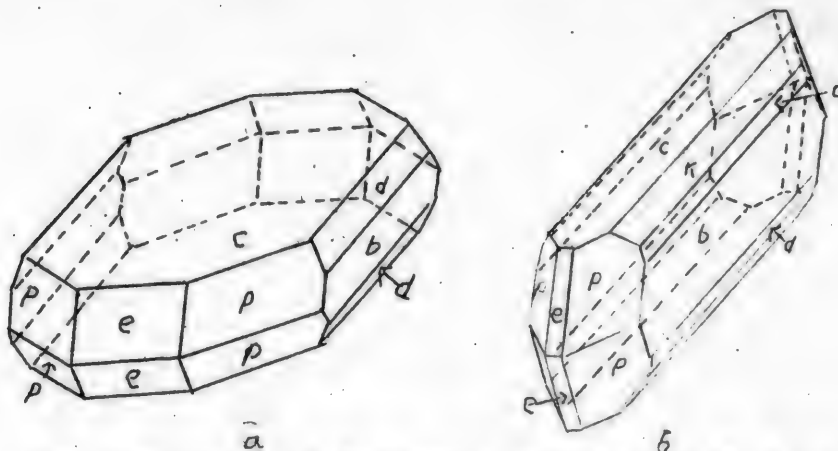


Fig. 2. Crystals of the rhombic modification of plumbic fluoride.

two habits, there were many which had strongly developed faces b [010], c [001], and d [011] in the direction of the a axis. The crystals which corresponded to these three most characteristic forms were grown from solutions of lead nitrate and ammonium fluoride. The use of lead acetate as a starting material gave crystals which had a greater development of the faces of the prisms of the first kind d [011] at the expense of the other faces. These crystals lacked the faces b [010] and c [001].

As has already been indicated the preparations obtained also contained crystals that differed sharply from the modifications of plumbic fluoride. These were the soft hexagonal plates. Qualitative chemical analysis of these crystals showed that in addition to lead fluoride they contained lead nitrate and water as well. Because of the comparatively small amount of these crystals, it was impossible to carry out a complete chemical analysis. In order to be able to come to even an approximate conclusion about these crystals, their composition was determined by an indirect method. For this purpose the amount of lead in the crystals was determined, as well as the loss on roasting, and the lead content in the residue after roasting. The results are given below (Table 2).

From these data and the lead content in pure plumbic fluoride (84.50%),

TABLE 2

	Percentage
Pb in crystals	80.07
Pb in residue of roasting	85.50
Losses in roasting (PbF_2 , PbO , H_2O , NO_2 , O_2)	6.01

assuming that roasting changes the lead nitrate into lead oxide, the composition of the crystals was calculated. It appeared to be: $\text{PbF}_2 \cdot 0.16\text{Pb}(\text{NO}_3)_2 \cdot 0.13\text{H}_2\text{O}$. As is evident, no definite chemical compound corresponds to this composition.

In order to obtain a more accurate picture of the nature of these crystals, roentgenograms were made. Judg-

ing the crystals from their external form to be hexagonal (the angles of the plates were 120° , but the side faces could not be measured), the network constants in the direction of the axes a and $b = a/\sqrt{3}$ were determined from the layer lines of the diagrams of single crystals as $a = 4.3 \text{ \AA}$; $b = 7.3 \text{ \AA}$. The photographs of the single crystals along the c axis were anomalous, i.e., without definite layer lines, so that in this direction it was impossible to determine the network constant.

As might have been expected, upon roasting (about 400°) the crystals were transformed into the cubic modification of plumbic fluoride. Roentgen photographs of the roasted crystals gave the diagram of single crystals. Thus, the small separate crystals after roasting were oriented in a single direction. During this process, the original crystal did not change in external appearance, but remained opaque and white.

If we calculate the network constants of the cubic modification of plumbic fluoride along the directions [101] and [112], they are 4.19 \AA and 7.26 \AA (calculated from the constant $a = 5.928 \text{ \AA}$ [1]).

Comparing these data with those for the Roentgen photographs, it is clear that the network of these crystals resembles the network of the cubic plumbic fluoride.

It further appeared, that after some time (about 2 or 3 months, or more) the crystals spontaneously gradually recrystallized to give the cubic or rhombic modification of plumbic fluoride.

Upon studying the crystals in polarized light, it was possible to observe the different anisotropic and isotropic places. Crystals of a completely uniform type were seldom encountered. From this it was possible to conclude that the process of recrystallization begins in these crystals from the very moment they are formed. Everything with regard to the constants of the crystals and their gradual recrystallization indicates their very close relation to the crystals of plumbic fluoride.

Judging from their composition, these crystals can be considered as mixed crystals of plumbic fluoride and plumbic nitrate. In the process of crystallization, the plumbic nitrate is here either adsorbed or located in the hollow spaces of the network of plumbic fluoride. As experiment shows, these mixed crystals were always formed during the growth of plumbic fluoride from the more concentrated solutions, when the velocity of formation of the crystals was great.

The specific gravity of plumbic fluoride was determined by the previously cited authors [1,3]. In view of the fact that these authors carried out their measurements on modifications from incompletely pure preparations, we redetermined the specific gravity. For purposes of measurement, we selected under the microscope crystals of the different modifications. The specific gravity was determined by a pycnometer in bromobenzene at a temperature of 25° . The values obtained for the two modifications were $d_{\text{cub.}} = 7.750$, $d_{\text{rhomb.}} = 8.445$.

These are somewhat greater than the values of the specific gravity obtained by Kolderup ($d_{\text{cub.}} = 7.0588$) and Schumann ($d_{\text{cub.}} = 7.070$, $d_{\text{rhomb.}} = 8.369$). This is due to the greater purity of the preparations we used. Ketelaar [2] in his work notes that the lead fluoride he obtained (rhombic modification) always contained traces of the cubic modification.

From the data in the literature it is clear that upon heating, the rhombic modification goes over into the cubic. With a change in temperature, the change of one modification into the other takes place only in a single direction. A temperature at which the rhombic modification changes to the cubic is given by all the authors cited [1,2,3]. According to Kolderup, this temperature is 400° , according to Ketelaar 200° , and according to Schumann 280° . It is clear from these data that the different authors give different transition temperatures. Using the separate modifications we had obtained, we determined the transition temperature anew.

The determination was carried out by gradually heating crystals of the rhombic modification in a small glass tube, placed together with a thermometer in a massive block of aluminum. The change in the crystals that took place upon heating was determined by investigating them under the microscope and by taking roentgenograms. It was thus found that the crystals of the rhombic modification begin to go over into the cubic at a temperature of 315° .

The transition temperature indicates that at high temperatures the cubic modification is the more stable.

However, the experiments on crystal growth showed that the cubic modification could be obtained even at room temperature. During these it appeared that the more slowly the growth of the crystals took place, the greater were the number of crystals of the cubic modification. Using extremely dilute solutions, it was possible to prepare crystals which consisted entirely of the cubic modification (octahedra). The quantity of crystals of the cubic modification was also increased when lead acetate was substituted for lead nitrate. On the other hand, preparations obtained after several weeks, by the diffusion of concentrated solutions contained no cubic modification at all. It follows from this that even at low temperatures under given conditions, the cubic modification can be very stable.

In conclusion, I wish to express my thanks to Prof. A. Keshan for his review of this work, and for the valuable suggestions he has made.

SUMMARY

1. The growth of crystals of plumbic fluoride by means of the diffusion of two solutions gives both the rhombic and cubic modifications. By altering the velocity of the reaction between the ions of lead and the ions of fluoride, it is possible to obtain either modification separately.

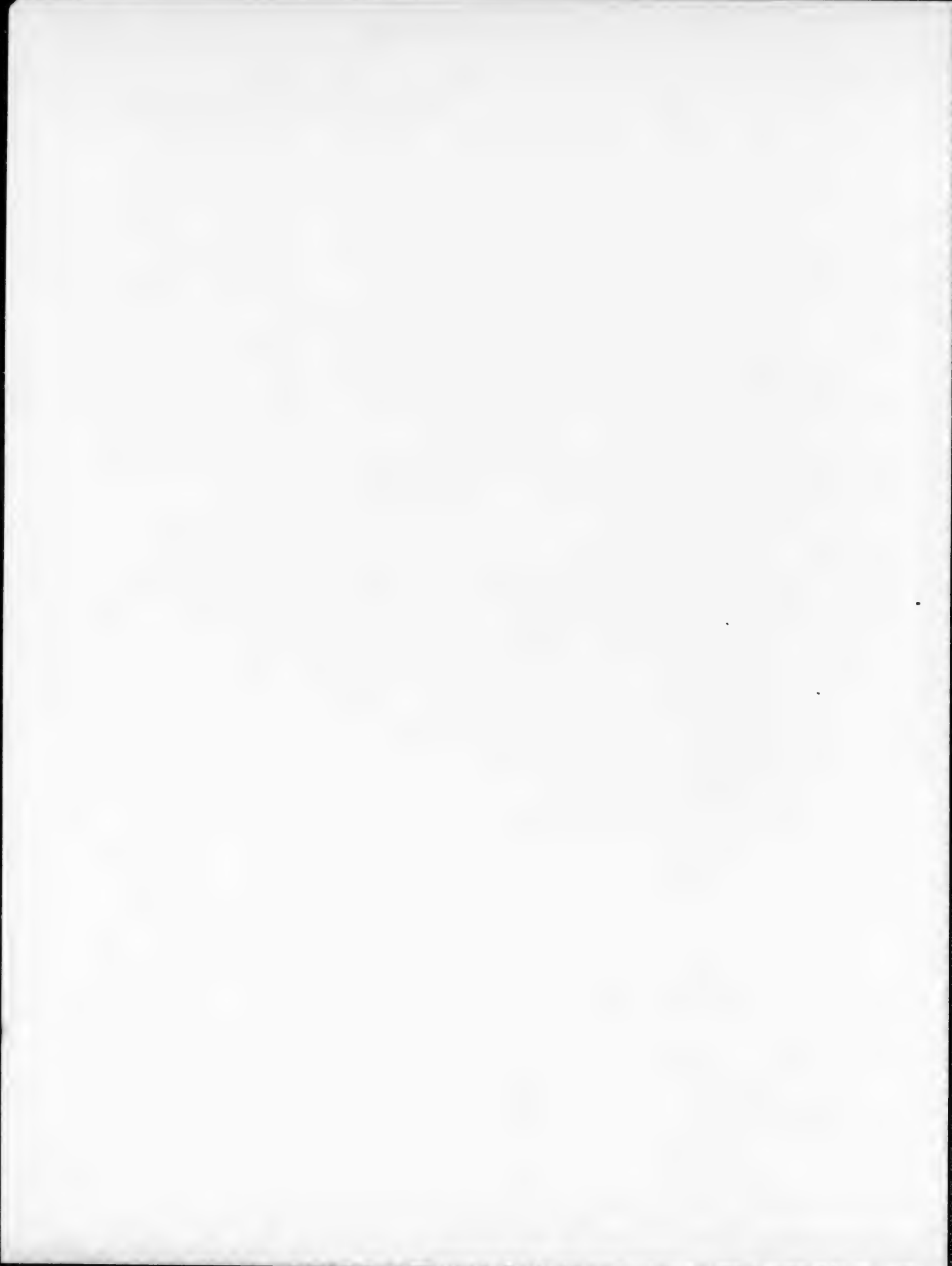
2. The crystals of the rhombic modification of plumbic fluoride belong to the class of rhombic dipyramids.

3. The growth of crystals of plumbic fluoride from solutions of plumbic nitrate and ammonium fluoride gives not only crystals of the cubic and rhombic modifications, but also mixed crystals of plumbic fluoride and plumbic nitrate. These mixed crystals are unstable, and gradually recrystallize to give the cubic or rhombic modification of plumbic fluoride.

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THE DIFFERENTIAL DETECTION OF CADMIUM

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It has been accidentally observed that the addition of a concentrated solution of potassium iodide to an ammoniacal solution of copper and cadmium ions results in the formation of a white precipitate which creeps along the walls. As this precipitate is doubtless of theoretical and practical interest, Prof. A.A. Tananayev suggested that I investigate both the composition of the precipitate and the possibility of utilizing it in chemical analysis.

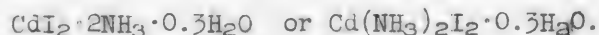
The literature gives no indication of the composition of the precipitate formed under the conditions of carrying out a qualitative analysis. In fact, Rammelsberg [1] and Tassilly [2] obtained $\text{CdI}_2 \cdot 6\text{NH}_3$ by heating dry CdI_2 in a current of NH_3 ; Dawson [3] obtained $\text{CdI}_2 \cdot 4\text{NH}_3$ by the absorption of NH_3 into an aqueous solution of CdI_2 containing an excess of NH_3 ; Rammelsberg and Tassilly [4] obtained $\text{CdI}_2 \cdot 2\text{NH}_3$ by heating solutions of CdI_2 with NH_3 , and $\text{CdI}_2 \cdot \text{CdO} \cdot \text{H}_2\text{O}$ from the mother liquor by the action of NH_3 on an ammoniacal solution of CdI_2 ; Grossmann [5] obtained a precipitate by prolonged boiling of concentrated NH_4I with $\text{Cd}(\text{OH})_2$, and Naumann [6] by passing NH_3 at 18° into a saturated solution of CdI_2 in acetone, ethyl acetate, and benzonitrile.

I therefore considered it advisable to investigate the composition of the precipitate which was obtained under the conditions of carrying out a qualitative analysis.

A precipitate was obtained by mixing a 0.1 N solution of cadmium nitrate, a concentrated solution of ammonia, and a saturated solution of potassium iodide (the latter may be replaced by the crystalline salt). The best results were obtained when to one millilitre of cadmium salt solution there were added 2 g of crystalline potassium iodide and 4 ml of concentrated ammonia. The completeness of the precipitation of the cadmium was confirmed by the use of ammonium or sodium sulfide.

The order of addition of the reagents influences the velocity of formation of the precipitate, especially at low concentrations of the cadmium ion. For example, if to the solution of cadmium salt the potassium iodide is first added, and then the ammonia, the precipitate forms more quickly than if the ammonia is first added to the solution of cadmium salt, and then the potassium iodide. A white finely crystalline precipitate separates, with the property of crawling along the walls. The precipitate is soluble in mineral and organic acids, in dilute and concentrated ammonia, in a saturated solution of ammonium chloride, and in a solution of potassium iodide. It is decomposed by water (during the decomposition, white flocs form), by ether ethyl alcohol, and a mixture of ethyl alcohol with water. Upon heating, it melts with the evolution of ammonia. Analysis of this compound gave the following figures: cadmium, 28.38%, iodide

62.11, ammonia 8%, water 1.51%.* The cadmium ion was determined as cadmium oxide, the iodide ion by volumetric analysis according to Volhard's method; ammonia was found by distillation into a solution of acid of definite strength and subsequent titration of the excess of acid with alkali. The formula that corresponds to this substance is:



Applying this reaction of the formation of an iodo-ammoniacal complex, under the optimal conditions indicated above, it is possible to detect 0.00023 g of cadmium (calculated as the metal) in one millilitre of solution of the pure cadmium salt after a 10 minute period. At first the solution becomes cloudy then the cloud grows more intense, and then a precipitate appears at the bottom of the test tube.

The formation of the iodo-ammoniacal complex may be used for the differential detection of the cadmium ion in a solution of mixed cations which does not contain the ions of tin, antimony, and arsenic acid. For this purpose, a small quantity of fine iron filings is added to the solution being tested, which is then boiled for 2 or 3 minutes, and filtered. To the filtrate, 5 ml of a concentrated solution of ammonia is added, and 0.5 to 1.0 ml of a 3% solution of hydrogen peroxide (to remove manganese); it is then heated and filtered. To the filtrate, 0.5 g of crystalline potassium iodide is added, the mixture vigorously shaken, and after being allowed to stand for 7 to 10 minutes, filtered through a dry filter which is as small as possible. The precipitate, unwashed, is dissolved on the filter in a small amount of 2 N nitric acid, then filtered into the same test tube where it was formed, and the filter washed with a small quantity of water. The solution must have an acid reaction (pH approximately 3; if the acidity is low, 2 N nitric acid is added). A current of hydrogen sulfide is passed through. The appearance of a canary-colored precipitate or a yellow cloud indicates the presence of the cadmium ion. It is thus possible to detect cadmium in 3 ml of a solution of the cations indicated above, with a content of 0.0007 g of cadmium ion calculated as the metal. With a lower cadmium content for instance 0.00037 g, a weak yellow cloud appears.

For the determination of the cadmium ion, the differential method requires about 20 minutes with a prepared solution.

SUMMARY

1. A differential reaction for the cadmium ion has been elaborated; it is based on the formation of an iodo-ammoniacal complex.
2. It has been found that the composition of the compound is $\text{Cd}(\text{NH}_3)_2\text{I}_2 \cdot 0.3\text{H}_2\text{O}$.
3. The sensitivity is $2.3 \cdot 10^{-4}$ g/ml. (calculated as metallic cadmium).
4. The determination of the cadmium ion requires 20 minutes with an already prepared solution.

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*Because of the difficulty of a direct determination the percentage of water was determined by difference.

THE NITRATION OF 2,7-DIMETHYLOCTANE BY NITROGEN DIOXIDE

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In accordance with our theory, the active agent in the nitration of the paraffin chain is nitrogen dioxide, and the reaction for the formation of the nitro-compound proceeds according to the scheme [1].



which is accompanied by the secondary formation of alkyl nitrites. Unless special measures are taken to preserve them, the alkyl nitrites are easily transformed into carboxylic acids and other oxidation and destruction products [5]. In conformity with these conclusions, we have shown by examples of the nitration of the paraffin chain of alkyl benzenes that the reaction for the preparation of mononitro derivatives can be carried out successfully under the usual conditions if nitrogen dioxide at high temperature is used as the nitrating agent, and oxygen is led into the reaction medium for the purpose of oxidizing the nitric oxide formed as a byproduct to the dioxide [2]. The present investigation was intended to show the applicability of this method for the preparation of mononitro paraffins.

As the compound to be investigated there was chosen the more or less accessible 2,7-dimethyloctane (diisoamyl); however, even in this case we were far from fulfilling one of the fundamental conditions for successfully carrying out the synthesis - the use of a very great excess of the hydrocarbon. All the same, the results obtained were fairly satisfactory. The suggested method of nitration of paraffins with nitrogen dioxide in the liquid phase has a number of advantages in comparison with the previously known methods of carrying out this reaction, especially as far as the simplicity of set-up and the small amount of time needed are concerned. With further development of this method it may be possible to attain still better results, if we utilize our data on the investigation of the preparation of phenylnitromethane [2]. In particular, there is no doubt that the reaction can be carried out with considerable success if instead of nitrogen dioxide nitric acid of sp. g. 1.5 is used. Everything said above permits us to express the confidence that the methods of nitration of the paraffin chain we have discovered will soon be utilized for purposes of preparation and research.

In conclusion, we should have liked to pay attention to the fact that the nitration of the paraffin chain in the liquid phase has an advantage over the carrying out of the reaction in the gas phase with respect to the velocity of reaction. The incomparably greater speed of the initial stage of reaction (1)

in the first case must be explained by the tremendous increase in the number of collisions of the hydrocarbon R - H and the monomer of nitrogen dioxide NO_2 in the liquid in comparison with the number in the gas phase. The number of collisions is increased not only because of the colossal increase in concentration of the hydrocarbon but also because of the somewhat greater concentration of nitrogen dioxide in the liquid phase. Most probably, there also takes place a decrease in the energy of activation. In the case of nitration of the nucleus of aromatic compounds the reaction has an ionic-complex character [3], and the reaction in the gas phase must take place very slowly.

EXPERIMENTAL

The original hydrocarbon was prepared according to the method of Wurtz, from isoamyl bromide. The first charge of the reaction flask consisted of fairly closely packed sodium wire and sufficient ether to cover it. The speed of the reaction was regulated by the speed of addition of the alkyl halide from a dropping funnel. In one operation, about 200 g of isoamyl bromide was treated. After the usual treatment and distillation, diisoamyl was obtained with b.p. 156° , and a yield of about 70% of theory. To purify it from unsaturated compounds, it was treated by mixing with sulfuric acid, washing, and redistillation.

The nitration of the diisoamyl was carried out in the apparatus which had been used to prepare phenylnitromethane [2]. In a flask were placed 150 ml of the hydrocarbon and 30 g of anhydrous copper sulfate; this was then heated on a boiling water bath while over a 4 hour period a mixture of 21.0 g of nitrogen dioxide (0.23 g-mol. N_2O_4) and 15 ml of diisoamyl was added. During this time, about 3 l. of oxygen was passed in.

After the reaction mixture had been washed with water, it was agitated with solutions of potassium bicarbonate and carbonate, which extracted about 1 g of carboxylic acids.

It was then extracted with 100 ml of 10% caustic soda, and carbon dioxide was passed into the extract until the latter was saturated. 16.6 g of the nitro product separated out. Subsequent acidification of the carbonate solution with acetic acid gave an additional 3.1 g of a thicker oil, and finally, treatment with hydrochloric acid gave approximately another 1 g of product.

The oil which had been separated out by carbon dioxide was distilled with steam. It gave 10.7 g of a nitro product, going over almost completely at 17 mm . residual pressure within the limits $124\text{--}129^\circ$; n_D^{20} of the distillate was 1.4431. It gave a sharp reaction for the formation of nitrolic acid and a scarcely noticeable one for the formation of pseudonitrol. In conformity with these results and the data of M.I. Konovalov [4], the product obtained consisted chiefly of 1-nitrodiisoamyl. The residue from the steam distillation was not investigated further.

After the extraction of the reaction mixture with alkali, diisoamyl was distilled off in vacuum, and the product which remained in the flask (about 19 g) was treated with a 40% solution of bisulfite; it gave 0.8 g of aldehyde probably 2,7-dimethyloctane aldehyde. The fractional distillation of the residue at a pressure of 22 mm gave the following fractions:

I	90-105°	2.4 g.
II	105-115°	2.2 g.
III	115-125°	1.9 g.
IV	125°	7.6 g; n_D^{20} 1.4371.
V	Residue	2.0 g.

The physical constants of the chief fraction (IV) were very close to the corresponding

data of Konovalov for tertiary nitrodiisoamyl (2-nitro-2,7-dimethyloctane). In the lower boiling fractions there were probably alcohols and their esters [5].

When the reaction was carried out at 130-140° with 40 ml of hydrocarbon and 20 ml of N₂O₄ it gave 0.8 g of carboxylic acids, 5.7 g of primary and secondary nitro compounds and 12.2 g of crude tertiary nitrodiisoamyl. Distillation of the latter product at 10 mm residual pressure gave the following fractions:

I	90-105°	3.1 g.
II	105-111°	4.8 g.
III	Residue	2.9 g.

The residue partially crystallized, and there could be isolated from it a small amount of pure crystalline 2,7-dinitro-2,7-dimethyloctane with m.p. 101°.

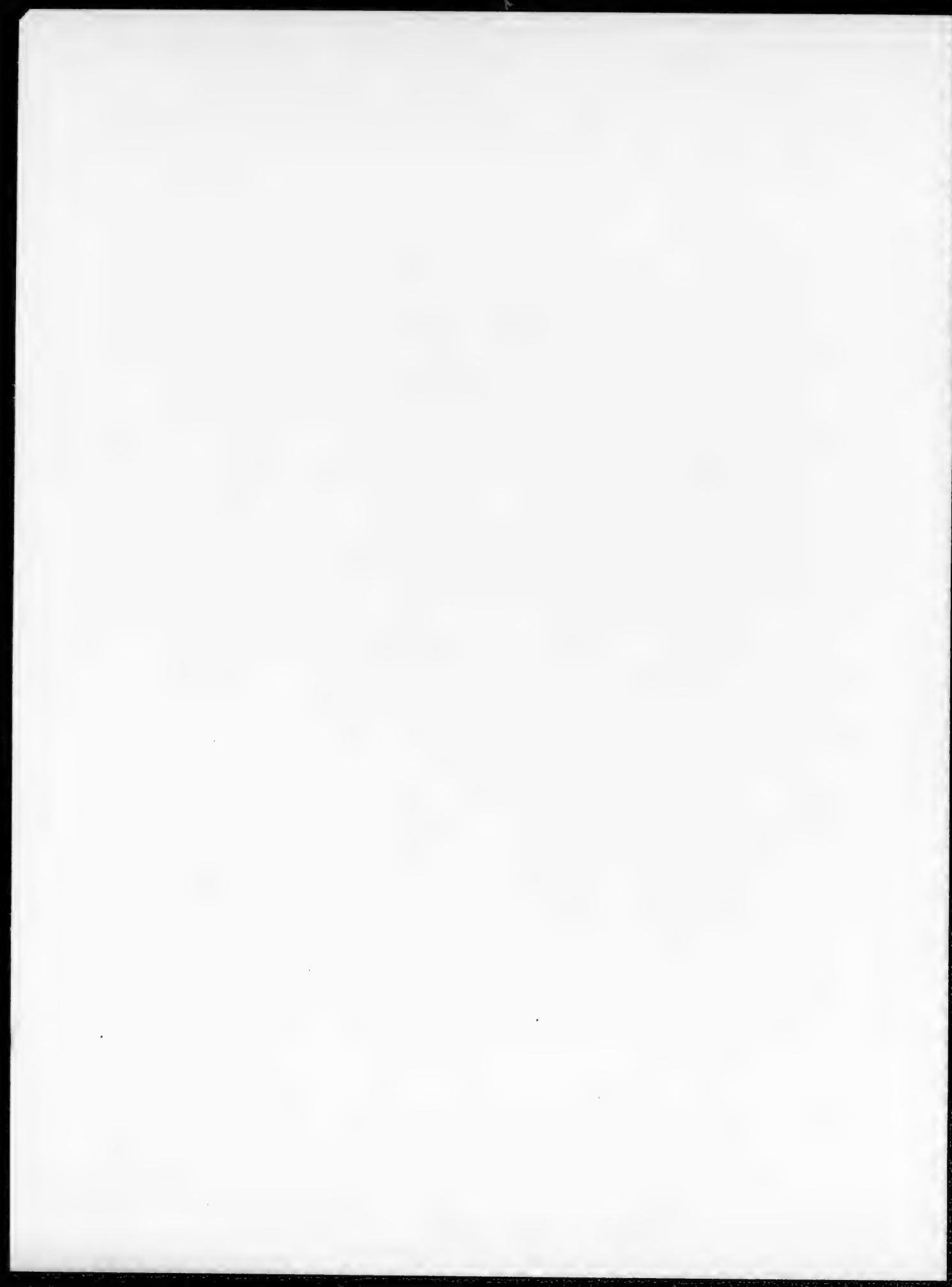
SUMMARY

On the basis of the nitration of 2,7-dimethyloctane with nitrogen dioxide in the liquid phase the applicability of the previously developed method for the nitration of the paraffin chain of alkyl benzenes has been shown for the paraffins themselves. The direction for further rationalization of this method of obtaining nitro paraffins has also been indicated.

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THE NITRATION OF n-HEPTANE AND 2,7-DIMETHYLOCTANE WITH NITRIC ACID

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The object of the present investigation was to give experimental evidence for one of the chief hypotheses of our theory of nitration of the paraffin chain - that the course of the reaction with nitric acid takes place through the intermediate reaction with nitrogen dioxide [1] - as applied to the paraffins themselves. The evidence was provided by carrying out parallel experiments on the action of nitric acid on paraffins in the absence and in the presence of nitrogen dioxide; in the case of 2,7-dimethyloctane, they supplemented the experiments on the action of nitrogen dioxide alone on the hydrocarbon.

In order to remove from one set of experiments the traces of nitrogen dioxide in the nitric acid, as well as the possibility of their increase in quantity as the reaction proceeded, we added urea nitrate in the experiments at ordinary temperature and ammonium sulfate in the experiments which involved heating. The results completely correspond to the theory. In the absence of nitrogen dioxide, nitric acid practically did not react with paraffins; the nitration with nitric acid took place only in the presence of nitrogen oxides but it took place best of all when only nitrogen dioxide was used, and no nitric acid was added.

From our experimental results, it also follows that nitric acid, even with sp. g 1.42, not only does not react with the paraffins by itself, but in addition does not result in any significant increase in the velocity of the action of the nitrogen dioxide with the paraffin chain (experiments with 2,7-dimethyloctane).

In accord with the theory, the nitration of 2,7-dimethyloctane took place much more easily than that of n-heptane, and could be carried out at ordinary temperatures. The reaction of the hydrocarbon with nitrogen dioxide gave approximately the same mixture of primary and tertiary nitrodisoamyls as nitration with nitric acid [2]. In this work, the oxidation products were not carefully investigated, and in addition to acids, only the formation of aldehydes was shown.

The nitration of n-heptane with nitric acid of sp. g 1.2, was successfully carried out, as a result of the addition of nitrogen dioxide, by heating in sealed tubes for 3 hours on the water bath, whereas Konovalov recommended for this purpose more extensive heating at 130° [3]. The data on the properties of the nitro product obtained permit us to consider it as identical with Konovalov's 2-nitropentane.

EXPERIMENTAL

Experiments with 2,7-Dimethyloctane

20 ml portions of the hydrocarbon were mixed with the nitrating agents and added substances and allowed to stand in conical flasks with ground-in calcium chloride tubes packed with anhydrous calcium nitrate. The time of standing was 50 days at 12 to 15°. After removal of the acid layer the reaction product was washed with water and then extracted by consecutive agitation with solutions of soda bisulfite, and finally alkali to which 1 ml of diethyl amine had been added in order to speed up the extraction of the primary nitrodiisooamyl. The product from the acidified soda extract was considered as 2,7-dimethyloctanoic acid, and the primary nitro compound was separated from the alkali extract by saturating with carbon dioxide - it gave a clear-cut reaction for the formation of nitrolic acid. Upon heating the bisulfite extracts of the 2nd and 3rd experiments with soda, there separated several drops of what smelled like 2,7-dimethyloctanal. After distillation of the excess of hydrocarbon, the residue was considered to be tertiary nitrodiisooamyl. Below are the data (cf. table) on the nitrating agents and the yields of reaction products; in the first experiment, 2 g of urea nitrate was added to the nitric acid for the reasons previously indicated.

Expt. No.	HNO ₃ (sp. g. 1.42) in ml	NO ₂	Yield (in g)		
			primary C ₁₀ H ₂₁ NO ₂	tertiary C ₁₀ H ₂₁ NO ₂	C ₉ H ₁₉ COOH
1	50				Traces
2	50	5	1.6	0.8	1.5
3		5	2.5	1.4	0.3

Experiments with n-Heptane

The charge of the tube in each of the two parallel comparison experiments consisted of 8 ml of heptane (5.8 g) with b.p. 97-98°, and 10 ml of nitric acid of sp. g 1.2 in one case (1) with the addition of about 1 g of nitrogen dioxide, and in the other (2) with 1.0 g of ammonium sulfate. The sealed tubes were heated in a horizontal water bath for 3 hours.

After the removal, in the first experiment from the organic layer of the excess of heptane there remained in the distillation flask 2.52 g of raw nitro product. Distillation at 40 mm residual pressure gave 1.37 g of a fraction boiling at 100-105°. At ordinary pressures this fraction boiled at 193-197° and gave a clear-cut reaction for secondary nitro compounds (formation of pseudo-nitrol), and a barely observable one for primary. These data permit us to conclude that the product we had obtained was identical with the 2-nitroheptane of Konovalov [3]. The residue from the vacuum distillation (1.06 g) was a thick, non-distillable oil. Evaporation of the residual nitric acid gave 0.8 g of an oily product that partially solidified; it contained apparently dicarboxylic acids.

In the second experiment in the absence of nitrogen oxides, no excessive pressure appeared in the tube and only traces of reaction product were obtained. When an attempt was made to carry out the reaction with nitric acid (sp. g. 1.3), the tube to which nitrogen dioxide had been added was shattered; in the experiment in which the ammonium salt had been added there was almost no additional pressure, and only traces of nitro products were obtained.

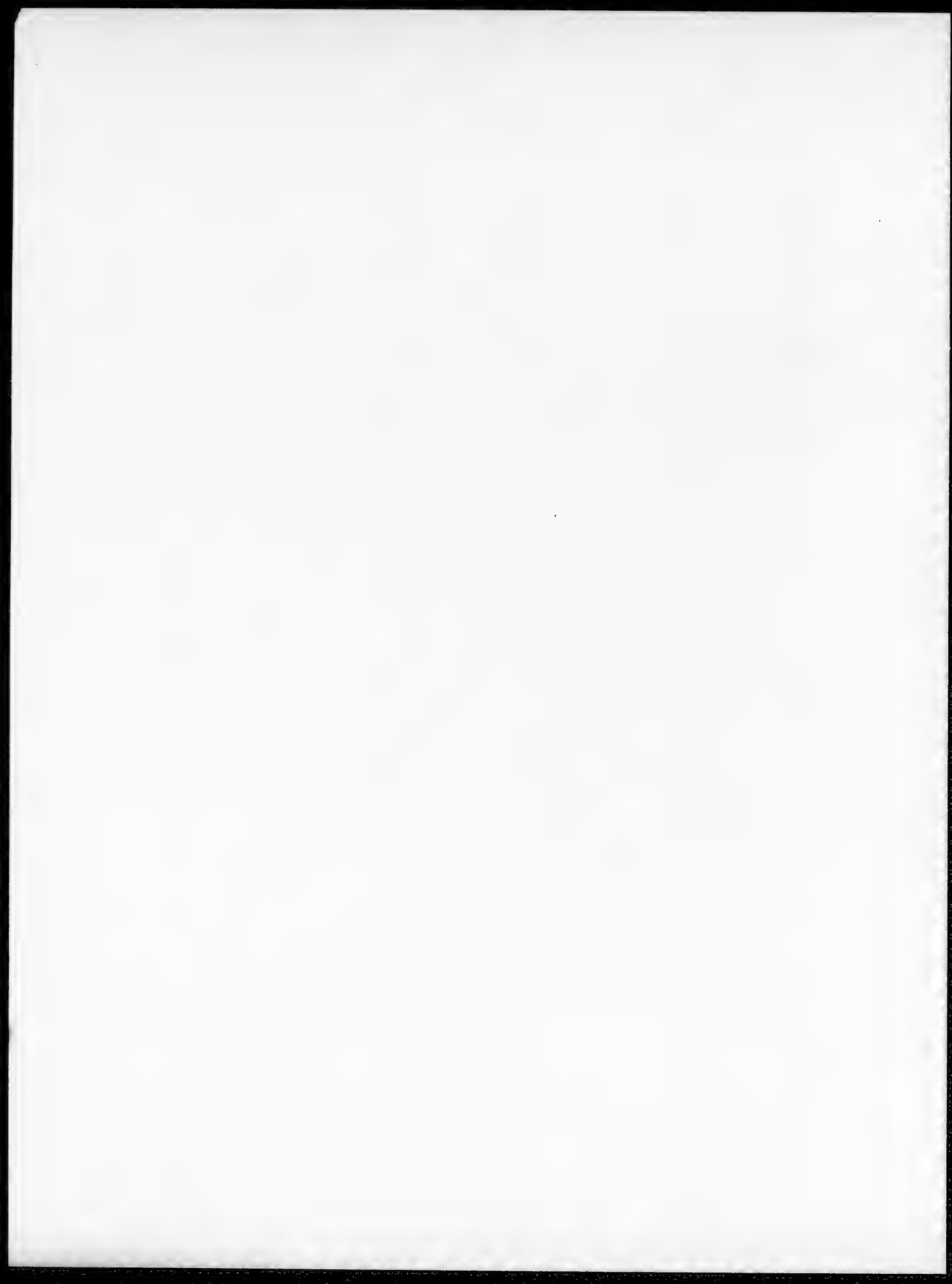
SUMMARY

It has been shown experimentally that the nitration and oxidation by nitric acid of paraffins of normal and iso structure takes place through the intermediate action of nitrogen dioxide; nitric acid of specific gravity up to 1.42 does not hasten the reaction between the paraffins and nitrogen dioxide.

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THE SULFONATION AND SULFONIC ACIDS OF ACIDOPHOBIC COMPOUNDS

VII. THE SULFONATION OF UNSATURATED HYDROCARBONS

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Works on the sulfonation of acidophobic compounds by pyridine-sulfotrioxide, begun in 1945 [1], showed by the example of five-membered heterocyclic systems, that this sulfonating agent was an excellent reagent for the introduction of sulfonic acid groups in compounds that were as sensitive to acids as pyrrol, furan, coumarone, etc.

Continuing our investigations, we attempted to broaden the field of application of pyridine-sulfotrioxide, and utilized it in order to sulfonate hydrocarbons. We tried about 50 individual hydrocarbons, of different types. The majority of them practically did not react without heating. Our experiments showed that the following were inert even upon long-continued heating up to 150°; paraffins (both those of normal and iso structure, such as isooctane); cycloparaffins (cyclohexane, methylcyclohexane, decalin); benzene and its homologs (toluene, durene, mesitylene, and pentamethylbenzene), in full agreement with the results of Baumgarten [2] and Terentyev [3]; other aromatic hydrocarbons (stilbene, anthracene, fluorene, triphenylethylene); mono-olefins (hexene-3, heptene-3, octene-2, nonene-4), i.e., those hydrocarbons whose double bond was not at the end of the chain.

The following reacted at 150° to a noticeable degree: α -olefins with a normal chain, such as hexene-1, and heptene-1. But the reaction proceeded slowly, gave low yields, and was accompanied by considerable darkening of the reaction mixture.

Hydrocarbons characterized by clearly expressed activity of the double bond entered into reaction fairly well even at 100°, to give good yields. Sulfonic acids were obtained from cyclohexene, methylenecyclohexane, camphene, styrene, and indene.

The reaction for the formation of sulfonic derivatives takes place through stages of the addition of two molecules of sulfuric anhydride at the double bond. In order to obtain the sulfonic acid salts, the sulfonated mass had to undergo further treatment by boiling with barium carbonate. Then, depending on the stability of the intermediate product, either the barium salt of the ethionic acid derivative was obtained, as with cyclohexene and methylenecyclohexane, or the splitting off of a molecule of sulfuric acid took place, and the barium salt of the unsaturated sulfonic acid was formed. This was observed in the cases of camphene, styrene, and indene.

EXPERIMENTAL

Starting materials. Pyridine-sulfotrioxide was prepared in the following manner. Solid sulfur trioxide was dissolved in dichloroethane. Then, with continual stirring and cooling, there was added an equivalent amount of pyridine, previously dried and distilled above barium oxide. The solid pyridine-sulfotri-

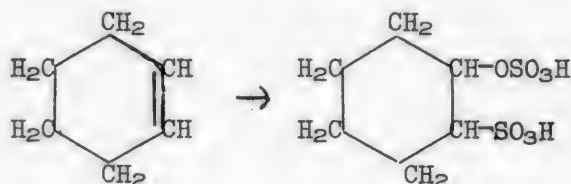
oxide which formed was filtered from the dichloroethane, and quickly dried in a desiccator at 100°.

The hydrocarbons to be sulfonated were dried and distilled before use. The fractions in the temperature intervals characteristic for the boiling points of the hydrocarbons were collected.

The method of sulfonation was uniform: the hydrocarbon was heated with three times the molecular quantity of pyridine-sulfotrioxide in a sealed glass tube for 10 hours at 100°. In case no reaction took place, the temperature was raised to 150°. A solvent was used during the sulfonation of solid and gaseous hydrocarbons. As solvent, carefully purified and dried dichloroethane was used.

Treatment of the sulfonation mixture. In those cases where the sulfonation took place, first of all the powdery pyridine-sulfotrioxide had melted and been converted into a viscous liquid of a color that ranged from yellow to dark brown. It solidified at room temperature. When the tubes were opened, no excess pressure was noted, nor the formation of sulfur dioxide. The reaction product was transferred to a flask, to which an excess of an aqueous suspension of barium carbonate was added. Then steam was passed through the flask. There distilled over with the steam pyridine and that part of the hydrocarbon which had not entered into reaction. The hydrocarbon was collected and its amount could be measured. The precipitate, of barium sulfate and excess barium carbonate, was filtered off and washed with hot water, and then treated with alcohol for the purpose of removing sulfones and other substances of a non-salt-forming character. The filtrate was concentrated to a small volume. The barium salt of the sulfonic acid was precipitated with methyl alcohol. The salt was washed several times with alcohol and dried in a desiccator at 70-80°. For purposes of analysis, the salt was reprecipitated from an aqueous alcohol solution, and heated, in order to remove water of crystallization, with benzene or toluene.

Cyclohexene:



From 2 g (0.023 g-mol) of cyclohexene and 11.5 g (0.069 g-mol) of pyridine-sulfotrioxide, 7.5 g of the barium salt was obtained:

4.522 mg substance: 2.640 mg BaSO₄.

Found %: Ba 34.85.

C₆H₁₀O₇S₂Ba. Calculated %: Ba 34.72.

Upon hydrolysis with 20% hydrochloric acid in a sealed tube for 2 hours at 150°, barium sulfate separated; no sulfur trioxide was observed.

Methylenecyclohexane. From 2 g (0.02 g-mol) of the hydrocarbon and 9.5 g (0.06 g-mol) of pyridine-sulfotrioxide, 4 g of the barium salt was obtained.

11.522 mg substance: 6.515 mg BaSO₄.

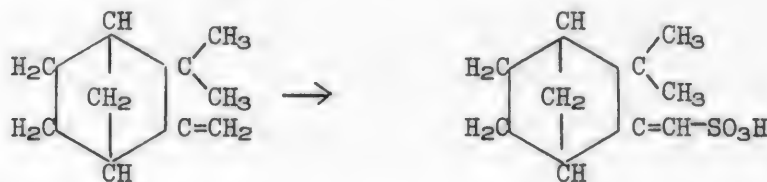
Found %: Ba 33.35.

C₇H₁₂O₇S₂Ba. Calculated %: Ba 33.27.

The salt resembled the previous salt in its properties. If the reaction took place according to the type that added to the double bond, the sulfonic acid group must be attached to the methylene group. However, it is possible that sulfonation was accompanied by preliminary migration of the double bond into the

ring to form methylcyclohexene-1, which has often been observed in methylenecyclohexane. A similar isomerization has been described by Suter [4] and his coworkers for the simplest olefins (propylene, isobutylene, etc.) in their investigation of the sulfonating action of dioxane-sulfotrioxide.

Camphene:



The sulfonation was carried out in dichloroethane solution. From 2 g (0.015 g-mol.) of camphene and 7 g (0.045 g-mol) of pyridine-sulfotrioxide, 4.5 g of the barium salt was obtained:

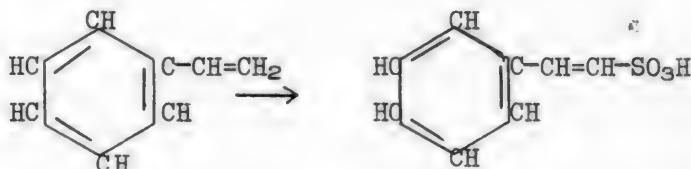
5.979 mg substance: 2.444 mg BaSO₄.

Found %: Ba 24.05.

(C₁₀H₁₅SO₃)₂Ba. Calculated %: Ba 24.15.

The salt was easily soluble in water. It decolorized bromine water, giving a precipitate soluble in alcohol. Heating with hydrochloric acid did not result in the formation of barium sulfate or the evolution of sulfur dioxide. We assume that the reaction proceeded in the method indicated, as it is known that it is precisely the methylene hydrogen atom in camphene that can be substituted by the nitro group or by bromine [5]. Like methylenecyclohexane, camphene has a semi-cyclic double bond; however, in this case there is no possibility of the bond's isomerizing into the ring.

Styrene:



The reaction took place as before. From 2 g of the hydrocarbon, 2.5 g of the barium salt was obtained. According to the analysis, it was the monosulfonic acid.

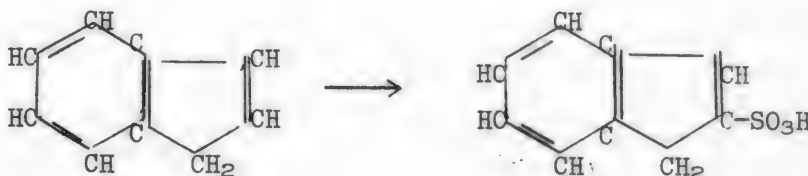
5.969 mg substance: 2.753 mg BaSO₄.

Found %: Ba 27.14.

(C₈H₇SO₃)₂Ba. Calculated %: Ba 27.27.

The structure, obviously, corresponds to the formula given, as the sulonic acids prepared by Quilico [6] by the sulfonation of styrene with sulfamic acid also have the same structure.

Indene:



The sulfonation of indene took place fairly smoothly at 100°. From 2 g of hydrocarbon, 2.5 g of the barium salt was obtained.

5.656 mg substance: 2.444 mg BaSO₄.

Found %: Ba 25.43.

(C₉H₇SO₃)₂Ba. Calculated %: Ba 26.02.

In the cold, the salt reacted easily with bromine water without giving barium sulfate. Upon heating with hydrochloric acid, hydrogen chloride apparently was added, as the solution no longer reacted with bromine water. Its composition corresponded to that of the monosulfonic acid. We assumed that the sulfonic acid group entered at position 2, and not in the methylene group. Fluorene, which has a similar group, could not be sulfonated at 100°, but upon heating to 150-160° for 10 hours underwent considerable darkening, with the evolution of sulfur dioxide. Apart from this, indene is a hydrocarbon similar to coumarone which is sulfonated [7] in the same way in the α -position.

We also conducted experiments on the sulfonation with pyridine-sulfotrioxide of diolefin hydrocarbons. Preliminary data indicate that a number of compounds of this type can be successfully sulfonated; we shall make our report with regard to these in our following communications.

SUMMARY

1. Pyridine-sulfotrioxide does not react (up to 150°) with paraffins, cycloparaffins, benzene homologs, or olefins which have the double bond on a non-terminal carbon atom.

2. α -Olefins (hexene-1, heptene-1) react at 150°.

3. We have prepared and described the barium salts of the sulfonic acids of cyclohexene, methylenecyclohexane, camphene, styrene, and indene.

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THE NITRATION OF n-PENTANE WITH NITROGEN DIOXIDE IN THE GAS PHASE

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The first report on the nitration of n-pentane in the gas phase by nitrogen dioxide was published by T. Urbansky and M. Slon in 1937 [1]. According to their brief data, the reaction was carried out in a tube at a temperature of about 200°, and gave the primary nitropentane and the 1,5-dinitro derivative.

We must note, however, that the boiling point they found for nitropentane (164-165° at 750 mm and 47-50° at 12 mm) did not correspond to their conclusions about its structure. About this time [2] we were elucidating the mechanism of nitration of saturated hydrocarbons, in accordance with which this reaction, both in the presence of nitric acid and of nitrogen oxides, takes place according to the same manner, to be precise:



The stable nitro compounds remain unchanged among the products of reaction, while the alkyl nitrites $RONO$ and the nitroso compounds RNO undergo various transformations, which have been previously considered in detail [3]. Nitric acid has no independent nitrating effect, and serves in this reaction only as a source for the formation of nitrogen dioxide, and a means for its progressive regeneration from the lower oxides.

It followed from our theory that the chief laws that regulated nitration with nitrogen dioxide and with nitric acid must be similar. Hence, it followed, in particular, that Konovalov's rule of the almost exclusive formation of secondary nitro compounds during the nitration of n-paraffins, which had been confirmed by our calculations of the energy of activation, must be applicable under the conditions of nitration described by Urbansky and Slon. At still higher temperatures, nitration can be carried out with the reaction tendencies of all the hydrogen atoms more or less equalized, and the formation of lower nitro paraffins [2,3].

The observed contradiction between the data of Urbansky and Slon and our theory and Konovalov's forced us even then (in 1938) to attempt an experimental test. In accordance with the results of our investigations (cf. experimental section), the nitration of n-pentane with nitrogen dioxide at 260-270° gives almost entirely the secondary nitro compound. We are forced to conclude that Urbansky and Slon also were dealing with the secondary nitropentane, and this is partially confirmed by the boiling point of the product they had obtained, and especially by its ~~value~~ under reduced pressure. It is possible that the failure to purify the

nitro compound by way of transforming it into a salt of the acyl form may have led the authors to an incorrect conclusion. We intended later to undertake a more thorough investigation of this reaction, but unfortunately, during the period that followed, this was impossible, and we are publishing the first results of the investigation.

We have shown recently that the nitration of n-pentane gives amyl nitrites and amyl alcohols [3]. Similar results have been obtained in the investigation of the nitration of cyclohexane.

EXPERIMENTAL

For purposes of nitration, Kahlbaum n-pentane was used, with b.p. 35.6-36.4°. The reaction was carried out in the apparatus shown in the sketch.

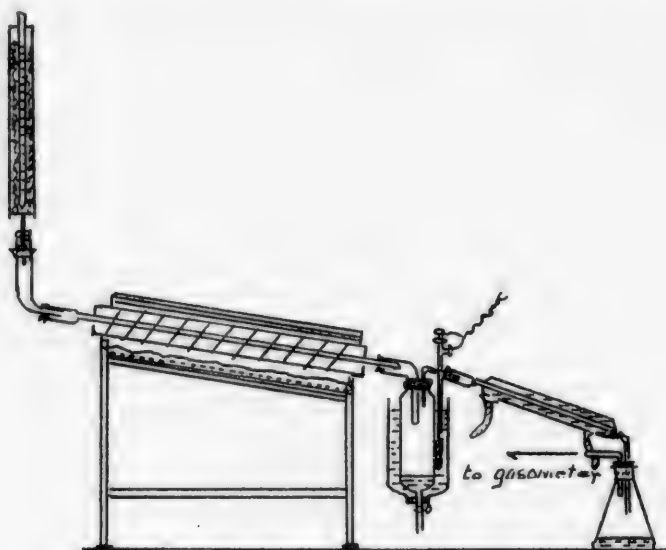


Fig. 1.

A mixture of 0.3 g-mol of pentane and 0.1 g mol of N_2O_4 was allowed to drop from a burette which was cooled with ice. The vapors formed were passed into the reaction tube, in which the temperature was maintained at about 260-270°. The velocity of input was regulated in such a way that the gas that left the reaction zone had a weak brown color. The vapors and gases were led into a separatory funnel, which was placed in a water bath at a temperature of 60°. Here the nitro products and dilute nitric acid were condensed. They were further passed through a water-cooled condenser and a receiver cooled with ice. Here the greater part of the unreacted hydrocarbon separated, along with a small quantity of water. The recovered hydrocarbon was supplemented to make up for the amount lost, NO_2 was added, and it was again used in the reaction.

1) In this way, 45 g of pentane were consumed during 8 hours of treatment in the apparatus, to give 21.2 g of raw nitroproduct, and 6.7 g of an aqueous layer. The formation during the reaction of a disproportionately large quantity of water in comparison with the yield of nitro products bears evidence for the preponderance in this case of the processes of profound oxidation of the hydrocarbon, probably, to CO_2 and H_2O .

2) Filling the tube with pieces of glass did not affect the velocity of

nitration and the composition of the product. This confirms both the absence of chains in the reaction, and the fact that it did not take place on a solid surface.

The reaction product was treated by agitation with water, then with 20 ml of a 20% potash solution, next with 10 ml of 40% sodium bisulfite, and finally again with water. The extracts had a deep brown-red color. The bisulfite extract was decomposed with soda and steam distilled; it gave a distillate in which the silver mirror test showed the presence of only traces of aldehydes.

In order to extract the nitro compounds, the residue from the reaction product was energetically shaken for 30 minutes with 20 ml of 28% caustic potash; during the shaking, the greater part of the organic layer passed into the alkaline solution, coloring it red-brown. Upon repeated shaking with 15 ml of caustic potash solution and 1 ml of diethyl amine, all the nitro product, with the exception of 0.7 g of residue, went to form a potassium derivative, whose solution this time was almost colorless. Upon saturating the first alkaline extract with boric acid, 10.8 g of nitropentane was obtained; upon treatment of its alkaline solution with nitrite and then (with cooling) with ether and acid, this gave a clear-cut reaction for a secondary nitro compound (formation of pseudo nitrol). Subsequent treatment of the aqueous alkaline solution showed the presence of only traces of a primary nitro derivative. The product distilled almost without a residue at about 45° and 10 mm residual pressure. Upon distillation at ordinary pressure, a little less than half the nitro product distilled at 151-153° (745 mm), the remainder at 153-156°. A similar treatment of the second alkali extract gave 3.6 g of nitro product, which distilled completely at 760 mm pressure within the range 156-158°; d_4^{20} 0.9479; n_D^{20} 1.4134; M_R 31.30.

All these physical and chemical data correspond to the secondary nitropentane. The literature gives for the secondary nitropentane b.p. 152-153° (746 mm) and for the primary 172° (760 mm). In accord with the general rules, n_D^{20} for the primary nitropentane is 1.4218, i.e., somewhat higher than that obtained for our isomer.

SUMMARY

In accord with our theory of the nitration of the paraffin chain and with M.I.Konovalov's rule, the nitration of n-pentane with nitrogen dioxide gives as the chief product of reaction the secondary nitropentane.

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THE USE OF DI-HALOGEN-SUBSTITUTED ETHERS FOR THE SYNTHESIS OF SYMMETRICAL DIMETHYLENEGLYCOL ETHERS

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The ethers of methylene glycol, as of the other glycols, have attracted and continue to attract at present the attention of investigators. The largest amounts of compounds containing oxygen in the chain that have been synthesized in the past years are related to the ethylene glycol or methylene glycol ethers. The glycol ethers increase the ability of a solution to undergo dilution, some of them have narcotic properties, and they are antidotes to strychnine; many natural perfumes and valuable alkaloids contain the methylene-dioxy grouping in their molecules. The glycol ethers, which have many valuable properties, have lately begun to acquire an important position in industrial organic chemistry. Their chief points of superiority are their complete neutrality and their great ability to mix with diluents. Much less attention has been paid to the synthesis of dimethylene glycol ethers. These ethers have been insufficiently investigated, with the exception of several works by Descude [1], who obtained, by the action of dichlorodimethyl ether and sodium methylate, the dimethyl ether of dimethylene glycol:



According to Descude's data, the dimethyl ether of dimethylene glycol boils at 106-108°, d_{20}^{20} 0.959. The diethyl ether of dimethylene glycol, obtained in the same way, boils at 140°. We obtained the diethyl ether of dimethylene glycol by another method [2,3]. We started with α, α' -dibromodimethyl ether, alcohol, and alkali. The reaction evolved a considerable quantity of heat, and was therefore conducted at low temperatures. It took place according to the following scheme:



This method is suitable for the preparation of ethers of methylene glycol of the simple and mixed type. The alkali which takes part in the reaction is needed, first, to neutralize the gaseous hydrogen bromide evolved, and second, to absorb the water which is given off.

As a result of these experiments, we synthesized the diethyl, dioctyl, di-butyl, diisopropyl, and diisoamyl ethers of dimethyleneglycol.

EXPERIMENTAL*

1. The preparation of the diethyl ether of dimethylene glycol. A mixture

*Work for diploma by L. Kosheleva and K. Aliyeva, done in the school year 1944/45.

of 32 g of NaOH and 25 g of ethyl alcohol with b.p. 78° was placed in a round-bottomed flask fitted with a mechanical stirrer, a reflux condenser, and a dropping funnel; it was cooled to -12°, and 40 g of dibromodimethyl ether with b.p. 150-151° was added drop by drop, with continual stirring. The ether was obtained by the method of Afishchenko [4].

After all the dibromodimethyl ether had been added, the mixture was stirred for another 30 minutes and allowed to stand for a day. Because of the comparatively high solubility of the product in water, the contents of the flask were filtered and distilled at ordinary pressure (25 g of crude product was obtained), dried over Na_2SO_4 to give 24 g of product, and then redistilled. Most distilled over at 140-141°. The liquid obtained had a pleasant odor, and the following characteristics:

d_4^{25} 0.922; n_D^{25} 1.3888; n_D^{20} 1.3892; MR_D 34.44.

$\text{C}_6\text{H}_{14}\text{O}_3$. Calculated: MR_D 34.837.

Literature data [1]: b.p. 140°; d_4^{25} 0.90781; n_D^{25} 1.38731.

2. Preparation of the dibutyl ether of dimethylene glycol. A mixture of 16 g of dry powdered NaOH and 16 g of butyl alcohol with b.p. 117° was placed in a round-bottomed flask fitted with a reflux condenser, a dropping funnel, and a mechanical stirrer with mercury seal, and cooled to -12°; over a period of 25 minutes 20.4 g of dibromodimethyl ether were gradually added drop by drop, with continuous mechanical stirring. A vigorous reaction took place with the evolution of heat. After the addition of all the dibromodimethyl ether, the mixture was stirred for another 40 minutes, and allowed to stand for a day. It was then heated on the water bath to 55-65° with constant stirring.

At the end of the reaction (which was indicated by the disappearance of the odor of the dibromodimethyl ether), the contents of the flask were cooled and diluted with 50 ml of water. Two layers formed: the upper, yellow, layer was ethereal, the lower was an aqueous layer. The upper layer was separated from the lower, washed with water, and dried. There was finally obtained 15 g of product. The liquid was fractionated in vacuum:

1st fraction with b.p. 46-72° at 6 mm 5 g,

2nd fraction with b.p. 72-79° at 6 mm 6 g,

Residue 3 g.

The 2nd fraction with b.p. 72-79° at 6 mm was subjected to analysis:

d_{20}^{20} 0.8619; n_D^{20} 1.4080; MR_D 54.4.

$\text{C}_{10}\text{H}_{22}\text{O}_3$. Calculated: MR_D 53.3.

0.1536 g substance: 14.3044 g benzene: Δt 0.29°.

Found: M 188.87.

$\text{C}_{10}\text{H}_{22}\text{O}_3$. Calculated: M 190.

The dibutyl ether of dimethylene glycol was a transparent liquid, insoluble in water.

0.1547 g substance: 0.3580 g CO_2 ; 0.1616 g H_2O .

0.1353 g substance: 0.3140 g CO_2 ; 0.1413 g H_2O .

Found %: C 63.10, 63.27; H 11.60, 11.60.

$\text{C}_{10}\text{H}_{22}\text{O}_3$. Calculated %: C 63.15; H 11.58.

3. The preparation of the dioctyl ether of dimethylene glycol. A mixture of 16 g of NaOH and 27 g of octyl alcohol was placed in a round-bottomed flask, fitted with a reflux condenser, a mechanical stirrer, and a dropping funnel, and cooled to -10°; 20.4 g of dibromodimethyl ether were then added drop by drop over a 30 minute period, with continuous stirring. After the addition of all the dibromodimethyl

ether, the mixture was stirred for another 30 minutes, allowed to stand a day, and then heated on the water bath for 1.5 to 2 hours at 55-65°. At the end of the reaction, the contents of the flask were cooled and diluted with water. The upper, ethereal layer separated from the lower, aqueous one. The upper layer was washed with water, and then gave a syrupy liquid with a lemon color. This was dried over Na_2SO_4 and subjected to distillation in vacuum.

The following fractions were obtained:

1st fraction with b.p.	64-84°	at 4 mm	3.5 g,
2nd fraction with b.p.	85-136°	at 4 mm	10 g,
3rd fraction with b.p.	137-147°	at 4 mm	14 g,
Residue			1.5 g.

The second and 3rd fractions were subjected to a second fractionation in vacuum at 2 mm:

There were obtained:

1st fraction with b.p.	57-134°	4 g,
2nd fraction with b.p.	135-142°	13 g,
Residue		3 g.

The substance with b.p. 135-142° was subjected to analysis:

d_{20}^{20} 0.8518; n_D^{20} 1.4300; MR_D 90.18.

$\text{C}_{18}\text{H}_{38}\text{O}_3$. Calculated: MR_D 90.25.

The dioctyl ether of dimethylene glycol was a colorless oily liquid, insoluble in water; it had a pleasant odor.

0.1227 g substance: 0.3218 g CO_2 ; 0.1398 H_2O .

0.1317 g substance: 0.3452 g CO_2 ; 0.1497 H_2O .

Found %: C 71.47, 71.48; H 12.65, 12.62.

$\text{C}_{18}\text{H}_{38}\text{O}_3$. Calculated %: C 71.52; H 12.58.

4. The preparation of the diisopropyl ether of dimethylene glycol. To 27 g of powdered NaOH which had been cooled to -10°, 40 g of isopropyl alcohol with b.p. 82° was gradually added; then, with constant stirring, 68 g of dibromomethyl ether was added drop by drop. The mixture was stirred for about 30 minutes and was allowed to stand for a day. It was next heated on the water bath to 50-60°, with continuous stirring; during this, the white precipitate was changed into a brown one. After cooling, 60 ml of water was added. The product was fractionated in vacuum, and a colorless liquid with a pleasant odor was obtained.

B.p. 30-32° at 15 mm; d_{20}^{20} 0.876; n_D^{20} 1.3883; MR_D 43.86.

$\text{C}_8\text{H}_{18}\text{O}_2$. Calculated: MR_D 44.073.

0.2 g substance; 22.073 g benzene: Δt 0.29°.

Found: M 162.

$\text{C}_8\text{H}_{18}\text{O}_3$. Calculated: M 158.8.

0.1317 g substance: 0.2861 g CO_2 ; 0.1327 g H_2O .

0.1643 g substance: 0.3569 g CO_2 ; 0.1653 g H_2O .

Found %: C 59.24, 59.23; H 11.19, 11.25.

$\text{C}_8\text{H}_{18}\text{O}_3$. Calculated %: C 59.29; H 11.11.

5. The preparation of the diisoamyl ether of dimethylene glycol. To a mixture of 45 g of isoamyl alcohol with b.p. 128-129° and 25 g of alkali at -10°, 51 g of dibromodimethyl ether was added drop by drop over an hour period with constant

stirring. The mixture was then stirred for an additional 30 minutes and allowed to stand for a day. After a day, it was heated on the water bath at 55-65° with constant stirring. After cooling, it was diluted with 50 ml of water. The usual treatment was followed by distillation in vacuum. This distillation gave a fraction with b.p. 68-70° at 4 mm in the form of a liquid with a pleasant odor.

d_{20}^{20} 0.860; n_D^{20} 1.4093; MR_D 62.709.

$C_{12}H_{26}O_3$. Calculated: MR_D 62.545.

0.200 g substance; 19.505 g benzene: Δt 0.24°.

Found: M 216.6.

$C_{12}H_{26}O_3$. Calculated: M 218.

0.2018 g substance: 0.4880 g CO_2 ; 0.2178 g H_2O .

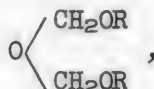
0.1823 g substance: 0.4408 g CO_2 ; 0.1962 g H_2O .

Found %: C 65.90, 65.82; H 11.99, 11.95.

$C_{12}H_{26}O_3$. Calculated %: C 66.05; H 11.92.

SUMMARY

1. The experimental data obtained permit us to draw the conclusion that the interaction of dibromodimethyl ether with alcohols gives ethers of dimethyl glycol:



where R can have either the normal or the iso structure.

2. Using the method described, the diethyl, dibutyl, dioctyl, diisoamyl, and diisopropyl ethers of dimethylene glycol have been synthesized.

3. It has been shown that an increase in the molecular weight of the symmetrical ethers of dimethylene glycol results in a decrease in their specific gravity.

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THE ADDITION OF HYDROGEN TO ACETYLENE DERIVATIVES

THE CATALYTIC HYDROGENATION OF METHYLETHYL(1-HYDROXYCYCLOPENTYLACETYLENYL) CARBINOL

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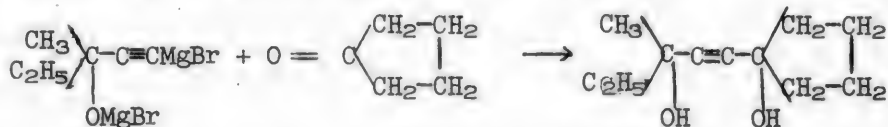
In studying the hydrogenation of acetylene derivatives, Yu. S. Zalkind [1] expressed the hypothesis that the velocity of addition of hydrogen to acetylene derivatives of γ -glycols in the presence of colloidal palladium is influenced not only by the weight and volume of the radicals in the glycol molecule but by their spatial structure as well.

It is known that the velocity of the addition of hydrogen to tetramethylbutinediol in the presence of colloidal palladium differs sharply from the velocity of addition of hydrogen to tetraethylbutinediol; the tetramethylbutinediol quickly adds two atoms of hydrogen, and then the velocity of addition takes a sharp drop, but in the case of tetraethylbutinediol, the addition of hydrogen proceeds very slowly.

Yu. S. Zalkind explained this sharp decrease in the velocity of addition of hydrogen by the fact that the long radicals, which have swung over toward the carbons joined by triple bonds, make the approach of the hydrogen toward these carbons more difficult.

In order to test this hypothesis again, we decided to investigate the hydrogenation of a glycol with an asymmetrical structure, methylethyl (1-hydroxycyclopentylacetylenyl) carbinol (I), whose molecular weight is comparatively close to that of tetraethylbutinediol, but has a quite different spatial structure.

Methylethyl (1-hydroxycyclopentylacetylenyl) carbinol was synthesized by the method of V.K.Teterin and A.P.Ivanov [2]; more exactly, by the action of the magnesium organic derivative of methylethylacetylenyl carbinol on cyclopentanone. There was thus obtained a new acetylenyl glycol in a yield of 43 to 45% of the theoretical.



The glycol was in the form of white crystals with m.p. 50-52°. With regard to catalytic hydrogenation, methylethyl (1-hydroxycyclopentylacetylenyl) carbinol behaves like the other ditertiary acetylenic γ -glycols: in the presence of colloidal palladium, the velocity of addition of hydrogen falls sharply after the addition of two atoms, and the further addition of hydrogen takes place slowly and uniformly. In the presence of platinum, it easily and uniformly adds 4 atoms of hydrogen, and a glycol of the saturated series is obtained.

Having studied the influence of the nature of the catalyst, the temperature, and other factors, for purposes of comparison we hydrogenated, on the same day, using a catalyst of the same batch (colloidal palladium, prepared on wheat starch)

tetramethylbutinediol and methylethyl (1-hydroxycyclopentylacetylenyl) carbinol (see table).

Glycol	Reaction Temp, °	Amount			Time of addition, minutes
		Glycol	Solvent	Palladium (in mg)	
Tetramethylbutinediol	18	0.01	50	10	6
Methylethyl-(1-hydroxycyclopentylacetylenyl)-carbinol	18	0.01	50	10	9

The results of the hydrogenation of tetramethylbutinediol, dimethyldiethylbutinediol, and methylethyl-(1-hydroxycyclopentylacetylenyl)-carbinol show that the introduction of the ethyl radical considerably reduces the velocity of addition of the hydrogen. In other respects, the glycol we have chosen, the still uninvestigated asymmetrical methylethyl-(1-hydroxycyclopentylacetylenyl)-carbinol, behaves just like the other ditertiary γ -acetylene glycols, i.e., in the presence of palladium, after the addition of two atoms of hydrogen, the velocity of hydrogenation decreases sharply. With an increase in the amount of palladium, the velocity of hydrogenation increases, and in the presence of platinum black, hydrogenation proceeds uniformly to the end.

EXPERIMENTAL

Preparation of Methylethyl-(1-hydroxycyclopentylacetylenyl)-carbinol

To a solution of ethylmagnesium bromide, prepared from 12 g of magnesium and 55 g of ethyl bromide, 23 g of methylethylacetylenyl carbinol was added, with careful cooling and stirring over a 2 hour period. The mixture was heated for 20 minutes on the water bath and allowed to stand for 3 to 4 hours; then, with cooling, 27 g of cyclopentanone was added over a 2 hour period and allowed to stand for 24 hours. The product was decomposed with moist ether. After the distillation of the ether, there remained an oil which gave a precipitate with an ammoniacal solution of silver oxide, thus showing the presence of unreacted alcohol. The acetylene alcohol was distilled off with steam. The thick viscous mass that was left was treated with ether. After the ether extract had been dried over calcined sodium sulfate and the ether distilled off, there was obtained a glycol with m.p. 50-52°. Yield 19 g, 43.7% of the theoretical. The glycol was very soluble in organic solvents.

0.1338 g substance: 0.3545 g CO₂; 0.1178 g H₂O.

0.0122 g substance; 0.1836 g camphor: Δt 19.8°

0.0126 g substance; 0.1504 g camphor: Δt 20°.

Found %: C 72.224; H 9.782; M 180.2; 183.

C₁₁H₁₈O₂. Calculated %: C 72.53; H 9.83; M 182.

0.089 g substance: 22 ml CH₄ (734 mm, 18°).

0.0769 g substance: 21.6 ml CH₄ (734 mm, 18°).

C₁₁H₁₈(OH)₂. Calculated: 22.5, 21.62 ml CH₄.

The Catalytic Hydrogenation of Methylethyl-(1-hydroxycyclopentylacetylenyl) Carbinol

Colloidal palladium (on wheat starch) was used as a catalyst. In 1 ml of an aqueous solution, there was 1.35 mg of palladium; the activity of the catalyst was tested by hydrogenating tetramethylbutinediol; for 0.01 g-mol of this glycol, the reaction required 6 minutes.

In order to show at a glance the behavior of the glycol upon hydrogenation,

we give the following examples:

Experiment 1. 1.82 g of glycol (0.01 g-mol), 10 mg of palladium, 50 ml of alcohol, P = 732 mm, T 18°, H₂ 248 ml.

t	3	6	9	12	15*
v	168	72	6	4	2
V	168	240	246	248	250
% H ₂	67.7	96.17	—	—	—

Experiment 2. 1.82 g of glycol (0.01 g-mol), 150 ml of alcohol, 10 mg of palladium, H₂ 248, T 19°, P 731 mm.

t	3	6	9	12	15
v	140	83	22	4	2
V	140	223	245	249	251
% H ₂	56.4	89.9	98.8	—	—

As can be seen from the data listed above, methylethyl-(1-hydroxycyclopentylacetylenyl)-carbinol behaves exactly like the other ditertiary acetylenic glycols, and after the addition of two atoms of hydrogen the addition reaction decreases sharply in velocity.

In the hydrogenation of methylethyl-(1-hydroxycyclopentylacetylenyl)-carbinol with platinum black, the course of the reaction was completely different. It proceeded uniformly, without a break.

Experiment 3. 0.91 g of glycol (0.005 g-mol), 0.7691 g of platinum black (prepared according to the method of Lev and Willstatter) 25 ml of alcohol, P 731, T 18°, H₂ 248 ml.

t	3	6	9	12	15
v	80	77	43	24	22
V	80	157	200	224	246
%H ₂	32.2	63.3	80.6	90.3	99.2

The Hydrogenation Products of Methylethyl-(1-hydroxycyclopentyl-acetylenyl) Carbinol.

After the addition of two atoms of hydrogen to methylethyl-(1-hydroxycyclopentylacetylenyl) carbinol, in order to isolate the ethylene glycol, the alcoholic glycol solution was filtered to remove the colloidal palladium. The alcohol was then driven off, and the residue began to crystallize in needle-shaped crystals. After recrystallization from benzene, they melted at 54-56°.

0.1046 g substance: 0.275 g CO₂; 0.1134 g H₂O.

0.1186 g substance: 0.3148 g CO₂; 0.1044 g H₂O.

0.010 g substance: 0.1096 g camphor: Δt 20°.

Found %: C 72.26, 72.64; H 12.2, 9.7; M 182.5.

C₁₁H₂₀O₂. Calculated %: C 72.73; H 10.87; M 184.

0.0504 g substance: 14.2 ml CH₄ (22°, 731 mm).

C₁₁H₁₈(OH)₂. Calculated : 13.7 ml CH₄.

The saturated glycol was obtained after the hydrogenation of the acetylene glycol in the presence of platinum black, in the form of white crystals with m.p. 52-54°.

* t is time in minutes from the beginning of the experiment; v is the volume of hydrogen, in millilitres, absorbed from the time of the previous reading; V is the volume of hydrogen absorbed from the beginning of hydrogenation.

0.0690 g substance: 0.181 g CO₂; 0.080 g H₂O.
0.1110 g substance: 0.116 g camphor: Δt 20.7.
Found %: C 71.67; H 11.27; M 187.
C₁₁H₂₂O₂. Calculated %: C 70.96; H 11.82; M 187.
0.0440 g substance: 12.1 ml CH₄ (22°, 731 mm).
C₁₁H₂₀(OH)₂. Calculated: 11.8 ml CH₄.

SUMMARY

Methylethyl-(1-hydroxycyclopentylacetylenyl)-carbinol has been synthesized, and the product of its hydrogenation in the presence of colloidal platinum has been studied. This glycol is hydrogenated in the presence of colloidal platinum more slowly than tetramethylbutinediol, indicating the influence of the structure of the glycol on the velocity of hydrogenation.

A new ethylene glycol, methylethyl-(1-hydroxycyclopentylethylenyl)-carbinol, and a saturated glycol, methylethyl-(1-hydroxycyclopentylethyl)-carbinol, have been obtained.

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THE PHOTOREACTIONS OF METALLO-ORGANIC MERCURY COMPOUNDS IN SOLUTION

II. THE REACTIONS OF DIPHENYLMERCURY

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In a previous communication [1] we have described the photochemical reactions of diphenylmercury with different organic compounds. We made the assumption that it dissociated into the radicals C_6H_5Hg and C_6H_5 , which further reacted with the solvent. In our present communication, we present the results of our further investigation in this field. The reaction was carried out with halogen derivatives: bromoform, trichloroethylene, and tertiary butyl chloride.

The behavior of bromoform with diphenylmercury was investigated by Koton, Zorina and Osberg [2] by heating the components in a sealed tube to 130° , but no reaction took place between them.

Upon illumination with ultraviolet light, the reaction proceeds very easily, with a quantitative separation of phenylmercuric bromide.

We may assume that the phenyl radical will break either hydrogen or bromine away from bromoform, as the C-Br bond is weaker than C-Cl.

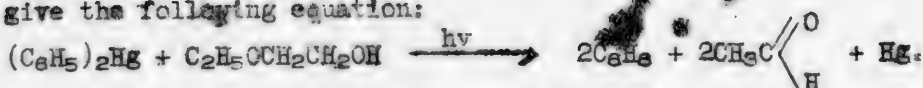
In the work of Kharasch [3] on the addition of chloroform and bromoform to double bonds, there were indications of the difference in the behavior of these substances. But under our conditions, this difference was not observed; in both cases, benzene was formed. Trichloroethylene was used in order to determine how an unsaturated halogen derivative would react. The photoreaction with diphenylmercury took place exactly as with chloroform, i.e., phenylmercuric chloride and benzene were obtained. It is of interest to note that tertiary butyl chloride, which has a more mobile chlorine atom, appeared extremely inactive. After very lengthy illumination, only a small amount of phenylmercuric chloride and metallic mercury separated. Of the solvents which did not contain halogen, representatives of the different classes of compounds were chosen: hydrocarbons, alcohols, ethers, and esters. Upon illuminating diphenylmercury in 2,2,4-trimethylpentane, a small quantity of mercury separated only after very lengthy illumination. In toluene solution, the separation of mercury took place fairly energetically, especially at the beginning of the experiment. Later on, the solution acquired a brown color, and the separation of mercury slowed down. The reaction gave a tarry mass, from which individual compounds were not isolated.

The photolytic decomposition of diphenylmercury in isopropyl alcohol took place exactly like the reaction with methanol, but the length of time required for the experiment was much greater. Benzene and mercury were isolated, and the formation of acetone was shown:



The reaction of diphenylmercury with ethyl ether took place very smoothly, with the formation of benzene and the separation of mercury. The formation of aldehyde was shown. Thus, for the reaction in the ethyl ether of ethylene glycol,

we may give the following equation:



In acetone and in ethyl formate, a quantitative formation of mercury and of benzene takes place, i.e., in these cases, hydrogen is split off from the solvent.

EXPERIMENTAL

Diphenylmercury and bromoform. 2.0 g of diphenylmercury in 15 ml of bromoform was illuminated for 12 hours. Red leaves of phenylmercuric bromide precipitated from solution. After recrystallization from dichloroethane, 0.55 g of phenylmercuric bromide was obtained, with m.p. 278°; there was no depression of the m.p. upon mixing with the pure product. The filtrate was distilled with steam, and the bromoform separated from the water and again distilled. A few drops of the distillate were diluted with carbon tetrachloride, and nitrated. m-Dinitrobenzene was obtained, with m.p. 90°, no m.p. depression with the pure substance. The residue after distillation with steam, to the amount of 1.4 g, was also phenylmercuric bromide, m.p. 277-278° from acetone, no m.p. depression with the pure substance. Thus, a total of 1.95 g of phenylmercuric bromide was obtained; this amounted to 96% of theory.

Diphenylmercury and trichloroethane. 1.5 g of diphenylmercury in 15 ml of trichloroethane was illuminated for 6 hours. Even a half hour after the beginning of illumination, the formation of the small red leaves of phenylmercuric chloride was noticeable. The residue was filtered and recrystallized from acetone; weight, 0.65 g, m.p. 257°, no m.p. depression upon mixing with the pure phenylmercuric chloride. The filtrate was distilled with steam and the distillate nitrated. m-Dinitrobenzene was obtained with m.p. 89°, no m.p. depression with the pure product.

A residue of 0.6 g, which did not come over with the steam, was recrystallized from acetone; it was phenylmercuric chloride, m.p. 257°, no depression with the pure substance. A total of 1.25 g of phenylmercuric chloride was isolated, amounting to 95% of theory.

Diphenylmercury and Tert.-Butyl Chloride. 1.2 g of diphenylmercury in 5 ml of tertiary butyl chloride was illuminated for 200 hours. The precipitate was separated from the solution, and washed with hot acetone, from which crystals of phenylmercuric chloride separated; these weighed 0.15 g. (15.5% of theory), and had m.p. 257°, no depression with the pure substance. The insoluble part was mercury (0.04 g, 6% of theory). After distillation of the solvent, 0.9 g of unreacted diphenylmercury remained in the residue, m.p. 125° after recrystallization from alcohol.

Diphenylmercury and 2,2,4-Trimethylpentane. 2.0 g of diphenylmercury in 15 ml of 2,2,4-trimethylpentane was illuminated for three weeks. Only a very small amount of metallic mercury separated. Most of the diphenylmercury remained unchanged.

Diphenylmercury and Toluene. 1.5 g of diphenylmercury in 10 ml of toluene was illuminated about 100 hours; other 0.5 portions of diphenylmercury were gradually added, until a total of 3.5 g had been allowed to react. Soon after the beginning of illumination, the separation of mercury began. The solution gradually darkened, and at the end of the experiment (100 hours) was dark brown. The toluene solution was distilled with steam. The residue was extracted with hot methanol; after cooling of the solution, 0.7 g of crystals of diphenylmercury (or 20%) separated, with m.p. 125°. After the extraction of the diphenylmercury, the residue

was a very thick brown mass, from which it was impossible to isolate individual compounds.

Diphenylmercury and Isopropyl Alcohol. 3.0 g of diphenylmercury in 10 ml of isopropyl alcohol was illuminated 240 hours. The metallic mercury was removed, and washed with hot isopropyl alcohol free from the undecomposed diphenylmercury. Weight of mercury, 1.4 g (82.3% of theory). The filtrate was distilled; 0.6 ml of benzol was obtained upon dilution of the distilled isopropyl alcohol with water. Nitration gave m-dinitrobenzene, with m.p. 90°, no depression with the pure substance. The reaction for acetone gave a positive result: the 2,4-dinitrophenylhydrazones of acetone melted at 125°. The residue from the distillation of the isopropyl alcohol and benzene was diphenylmercury, 0.5 g (16.7% of theory), with m.p. 124-125° after recrystallization from benzene; there was no m.p. depression with the pure substance.

Diphenylmercury and Ethyl Ether. 1.8 g of diphenylmercury in 10 ml of ether was illuminated for 40 hours. 0.9 g of mercury (90% of theory) was obtained. The ether was distilled off. There was a strong odor of acetaldehyde in the distillate, and the reaction for aldehyde (mirror) was positive. From the residue, 0.8 ml of benzene (90% of theory) was distilled with steam. After nitration, m-dinitrobenzene was obtained, with m.p. 91°, no depression with the pure substance.

Diphenylmercury and Ethyl Cellosolve. A solution of 1.0 g of diphenylmercury in 10 ml of the ethyl ether of ethylene glycol was illuminated for 25 hours and another 1.5 g of diphenylmercury was then added. The illumination was continued for 65 hours in all. 1.1 g of mercury (79% of theory) was obtained. From the solvent, 3 ml was distilled off, and upon dilution with water, this gave 0.6 ml of benzene (68% of theory). Nitration gave m-dinitrobenzene with m.p. 90°, no depression with the pure product. After removal of the benzene, the aqueous-alcoholic solution had a strong odor of acetaldehyde, and gave an aldehyde reaction. In the residue from distillation of the solvent, 0.5 g of diphenylmercury (20% of theory) was found; after recrystallization, it melted at 125° and gave no m.p. depression when mixed with the pure compound.

Diphenylmercury and Acetone. 1.5 g of diphenylmercury in 10 ml of acetone was illuminated for 25 hours; another 1.0 g of diphenylmercury was added. Illumination was continued for 50 hours. 1.0 g of mercury (72% of theory) was recovered. The acetone was distilled off and diluted with water to give 0.7 ml (57% of theory) of a benzene layer. The m-dinitrobenzene obtained by nitration had a m.p. of 89°, and gave no depression when mixed with the pure compound. Crystals of diphenylmercury separated from the residue after distillation of the acetone; after recrystallization from acetone, 0.4 g was obtained (16% of theory), with m.p. 125°, without m.p. depression when mixed with the pure product. After removal of the diphenylmercury, there remained a non-crystallizable yellow, viscous mass, which was not further investigated. It contained an additional small quantity of diphenylmercury (separation of phenylmercuric chloride was obtained with an alcoholic solution of HCl).

Diphenylmercury and Ethyl Formate. 1 g of diphenylmercury in 10 ml of ethyl formate was illuminated for 20 hours, and the separation of metallic mercury began almost at once. An additional 2 g of diphenylmercury was then added, after which the decomposition became noticeably slower. The reaction mixture was illuminated until no more diphenylmercury was decomposed. (This took about 100 hours). The metallic mercury was filtered off; it weighed 1.63 g (96% of theory). The filtrate was distilled on the water bath. The distillate was diluted with water and gave an almost quantitative yield of benzene - 1.6 ml. The benzene was nitrated to give m-dinitrobenzene, m.p. 89°, without depression when mixed with

the pure product. From the residue left on distillation on the water bath, 0.02 g of diphenyl was obtained; m.p. 69°, without depression when mixed with pure diphenyl.

SUMMARY

1. A solution of diphenylmercury in bromoform is decomposed upon illumination with ultraviolet light to give phenylmercuric bromide and benzene.

2. A solution of diphenylmercury in trichloroethylene gives, upon illumination, phenylmercuric chloride and benzene. The reaction proceeds rapidly, and with a quantitative yield.

3. Tertiary butyl chloride appears to be very inactive, and gives, after prolonged illumination, only an insignificant yield of phenylmercuric chloride.

4. In solvents which do not contain halogen (2,2,4-trimethylpentane, toluene, isopropyl alcohol, ethyl ether, ethyl cellosolve, acetone, and ethyl formate), the photodecomposition of diphenylmercury always gives benzene and metallic mercury. In a solution of 2,2,4-trimethylpentane the reaction takes place very slowly. Isopropyl alcohol and diphenylmercury give acetone. In ethyl cellosolve and ether, the reaction was shown to give aldehyde.

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* See CB translation p. 711 ff.

THE PHOTOREACTIONS OF METALLO-ORGANIC COMPOUNDS OF MERCURY IN SOLUTION

III. THE PHOTOREACTIONS OF DIBENZYL MERCURY

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In previously published work [1] we have indicated the great difference between diphenylmercury and dibenzylmercury when these compounds are heated under pressure with hydrogen, or with alcohols. In the case of diphenylmercury, benzene is formed and mercury separates, whereas dibenzylmercury in every case gives dibenzyl and mercury. The same difference is observed when these mercury compounds are heated with sulfur. The C_6H_5 radicals transfer to the sulfur to form $C_6H_5SC_6H_5$, while $C_6H_5CH_2$ radicals dimerize to give dibenzyl [2]. Under the influence of acids, diphenylmercury and dibenzylmercury react in the same manner, giving benzene or toluene respectively, plus $RHgX$.

The difference between the two types of reaction is explained by the fact that in the first type, dissociation into radicals takes place, while with acids an ionic mechanism comes into play.

The benzyl radical, in contradistinction to the phenyl, can be stabilized by resonance [3].

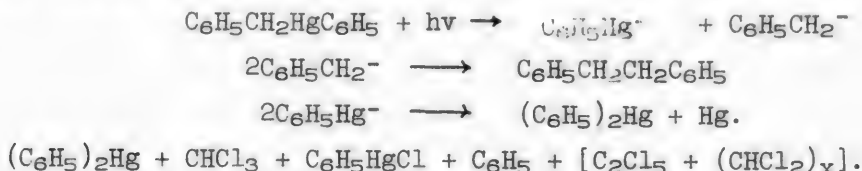


Thus, there exists the possibility of the radicals dimerizing.

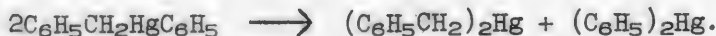
For the photoreaction of diphenylmercury [4] we suggested an analogous scheme by way of the primary formation of the phenyl radical. It may be supposed, therefore, that in the photoreaction dibenzylmercury gives dibenzyl. The photoreaction was carried out in methyl alcohol and in chloroform. With these two substances diphenylmercury gives a quantitative yield of benzene and mercury or C_6H_5HgCl . Dibenzylmercury, as was to be expected, gives, upon illumination in chloroform and methyl alcohol, dibenzyl, plus, in the former case, calomel, in the latter, mercury.

In order to compare the properties of the phenyl and benzyl radicals we carried out experiments with benzylphenylmercury. This mercury derivative was obtained by Hilpert and Grüttner [5], by the Grignard method. It was in the form of a yellow oil. We synthesized it by the much more convenient method of Freidlina, Nesmayanov, and Kocheshkov [6]. In chloroform solution, illumination gave mercury, dibenzyl, phenylmercuric chloride, and benzene.

The course of the reaction may be indicated in the following manner:



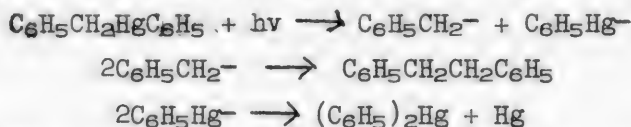
However, it is also possible to assume another mechanism, based on the initial symmetrization of benzylphenylmercury to give dibenzylmercury and diphenylmercury:



Each of the compounds formed then reacts further with chloroform independently. The first mechanism seemed to us more probable because of the following considerations: upon illumination, dibenzylmercury in chloroform solution forms calomel quantitatively, while benzylphenylmercury gives metallic mercury, no calomel at all being observed.

Benzylphenylmercury is only slightly soluble in methyl alcohol. At the bottom of the quartz test tube, in which the experiment was carried out, there remained an insoluble oil of benzylphenylmercury; therefore, the test tube was frequently shaken during the illumination. After some time, the oily drops were converted into a crystalline precipitate of diphenylmercury. Metallic mercury also separated. Dibenzyl was found in the alcoholic solution.

We may suggest the following reaction mechanism:



The diphenylmercury which separates out reacts further in its turn with the alcohol to give benzene, mercury, and formaldehyde.

EXPERIMENTAL *

Dibenzylmercury and Methyl Alcohol. 1.5 g of dibenzylmercury in 10 ml. of CH_3OH was illuminated for 50 hours. Mercury formed at the bottom of the test tube to the amount of 0.75 g., or 98% of theory. The alcohol was distilled off, and the residue steam-distilled; 0.55 g of dibenzyl (80 %) was obtained, with m.p. 53° , without depression when mixed with the pure compound.

Dibenzylmercury and Chloroform. 2.0 g of dibenzylmercury in 10 ml of CHCl_3 was illuminated for 40 hours. The precipitate which formed was filtered off from the chloroform solution and washed with chloroform. There was obtained 1.2 g of calomel, corresponding to 100% of theory. The chloroform was distilled off from the solution, and the residue distilled with steam. There was obtained 0.5 g of dibenzyl (theoretical amount) with m.p. 53° , with no depression upon mixing with pure dibenzyl. After distillation, a thick yellow oil which contained chlorine was obtained.

Benzylphenylmercury. The synthesis was carried out according to Nesmeyanov's method. To a boiling solution of 1.9 g of benzylmercuric chloride in 120 ml of alcohol, 5 ml of a 20% solution of NaOH was added, and a boiling solution of 1.0 g of $(\text{C}_6\text{H}_5)_2\text{SnCl}_2$ in 20 ml of alcohol. The hot mixture was filtered and diluted with an equal volume of water. The oil which separated was extracted with ether. The ether was distilled off in vacuum from the dried solution. There was obtained 1.8 g of benzylphenylmercury in the form of a thick oil, which was immediately used for the experiments.

Benzylphenylmercury and Methyl Alcohol. 1.8 g of benzylphenylmercury was illuminated for 25 hours in 10 ml of methyl alcohol. A precipitate of diphenylmercury formed at the bottom of the test tube. The precipitate was separated from the alcoholic solution and the diphenylmercury separated from the mercury by washing with hot acetone. There were obtained 0.55 g of mercury, or 57% of theory, and 0.60 g of diphenylmercury with m.p. $122-125^\circ$, with no depression upon mixing

* Student Ageyeva took part in this work.

with the pure compound. The yield of diphenylmercury equaled 70% of theory. The alcohol was driven off from the filtered solution. Upon dilution of the distillate with water, a faint cloudiness (benzene) formed. The residue from the distillation of the alcohol was distilled with steam. There was obtained 0.3 g of dibenzyl, a 68% yield, with m.p. 51°. There was no depression upon mixing with pure dibenzyl.

Benzylphenylmercury and Chloroform. 2.4 g of benzylphenylmercury in 10 ml of chloroform was illuminated for 25 hours. A precipitate of mercury and phenylmercuric chloride was formed. The precipitate was filtered off and treated repeatedly with hot acetone. After washing, 0.9 g of mercury was obtained, or 69% of theory. From the acetone solution, 0.59 g of phenylmercuric chloride was obtained, with m.p. 251°, and no depression upon mixing with the pure product. The yield equalled 58%. The chloroform solution was distilled, and the distillate nitrated. There was obtained 0.14 g of m-dinitrobenzene with m.p. 90°. The residue from the chloroform distillation was steam-distilled. From the distillate there was recovered 0.34 g of dibenzyl with m.p. 51°, with no depression upon mixing with pure dibenzyl. The yield of dibenzyl equalled 58%.

SUMMARY

1. Dibenzylmercury decomposes photolytically in chloroform and methyl alcohol to give dibenzyl plus calomel (in chloroform) or metallic mercury (in alcohol).
2. The photodecomposition of benzylphenylmercury in methyl alcohol proceeds according to the equation:



Upon further continuing the illumination, the diphenylmercury reacts with the alcohol to give mercury, benzene, and formaldehyde.

3. In the photolytic reaction with chloroform, benzylphenylmercury gives dibenzyl, mercury, phenylmercuric chloride, and benzene.

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SEVERAL DERIVATIVES OF 2-NAPHTHOL-4-SULFONIC ACID

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In a previous article on "Several Nitroso Compounds of the Naphthalene Series" [1], there was a brief reference to 1-nitroso-2-naphthol-4-sulfonic acid. In returning to the question of the properties of the nitrosonaphthols, we decided that it would be useful to give more precise data on our previous results and to supplement them somewhat. Of the methods given in the literature for the preparation of 2-naphthol-4-sulfonic acid, the reduction of 1-diazo-2-naphthol-4-sulfonic acid with an alkaline solution of stannous oxide was worthy of attention for laboratory purposes. This method, referred to by us in the article cited above, was described later [2], and directions were given for a method of preparation that was, in our opinion, not quite successful; our method is given below. The pure 2-naphthol-4-sulfonic acid and its salts are not described in the literature, which refers only to their exceedingly great solubility. We obtained the naphthol-sulfonic acid in the form of the sodium salt, which, as analysis showed, was isolated, depending on the conditions, with different amounts of water of crystallization. Upon nitrosation by the same method as is customary for other derivatives of 2-naphthol, it is transformed into 1-nitroso-2-naphthol-4-sulfonic acid. This nitroso compound possesses an exceedingly mobile sulfonic acid group. Thus, by the action of an aqueous solution of aniline or p-toluidine upon the aqueous solution of the sodium salt of the nitroso compound, 4-phenylamino and 4-p-tolylamino-1-nitroso-2-naphthol are obtained, and by brief heating of the nitroso compound with an approximately 1.5% solution of caustic soda, 1-nitroso-2,4-dihydroxynaphthalene is formed. Here, in the case of 1-nitroso-2-naphthol-4-sulfonic acid, which reacts with amines to give 4-arylamino-1,2-naphthoquinone, and is transformed by the action of caustic soda into 4-hydroxy-1,2-naphthoquinone [3]. The isomeric 2-nitroso-1-naphthol-4-sulfonic acid is stable under the action of more concentrated alkali [4].

EXPERIMENTAL

The Sodium Salt of 2-Naphthol-4-sulfonic Acid. To a solution of 362.5 g of 78.6% stannous chloride (1.5 mole) in 1000 ml of water, acidified with 50 ml of concentrated hydrochloric acid, at 3 to 14°, there is added over a period of 1.5 hours 830 ml of a concentrated solution of caustic soda (12.8 moles). To the brown solution, at 11 to 15°, there is added over a period of 1.5 hours, a suspension of 250 g of 1-diazo-2-naphthol-4-sulfonic acid (1 mole) in 300 ml of water. After the frothing has ceased, the solution is heated to 50°, and acidified with hydrochloric acid until it gives a weakly acid reaction. The tin oxide is filtered off and washed with water; the remaining tin is removed with hydrogen sulfide. According to the analysis (coupling with diazo-p-toluene) the yield of 2-naphthol-4-sulfonic acid consists of about 83% of the theoretical. Upon concentration of the solution, sodium chloride precipitates out; this is periodically filtered off and washed with alcohol. The highly concentrated solution, upon cooling, solidifies because of the precipitated sodium salt of the naphtholsulfonic acid.

The sodium salt is very soluble in water and in alcohol, and crystallizes

in two forms: upon rapid cooling of the aqueous solutions, it precipitates in the form of long needles with two molecules of water, and upon slow cooling in the form of regular hexagonal tablets containing one molecule of water. It also separates in the latter form from alcoholic solutions upon the addition of ether.

Analysis of the needle shaped crystals:

0.9118 g substance: loss in weight upon drying (120°),
0.2627 g dry substance: 0.0756 g Na₂SO₄. 0.1172 g.
Found %: H₂O 12.85; Na 9.32.
C₁₀H₇O₄SNa·2H₂O. Calculated %: H₂O 12.77.
C₁₀H₇O₄SNa. Calculated %: Na 9.33.

Analysis of the substance having the form of hexagonal plates.

0.9850 g substance: loss in weight upon drying (120°) 0.0684 g.
0.2640 g dry substance: 0.0760 g Na₂SO₄.
Found %: H₂O 6.94; Na 9.33.
C₁₀H₇O₄SNa·H₂O. Calculated %: H₂O 6.82.
C₁₀H₇O₄SNa. Calculated %: Na 9.32.

1-Nitroso-2-naphthol-4-sulfonic Acid. The solution of 61.5 g (0.25 mole) of the sodium salt of 2-naphthol-4-sulfonic acid and 18.1 g of sodium nitrite (5% excess) in 600 ml of water is cooled to -3°, and over a period of 5 hours there is added, below the surface of the liquid, 38 ml of hydrochloric acid with sp.gr. 1.12 which had been diluted with an equal volume of water; after stirring for an additional three hours, the mixture is allowed to stand for 10 hours. The precipitate is filtered off and washed with a solution of salt and alcohol. Yield 62.2 g, i.e., 92% of the theoretical. The sodium salt of the nitroso compound crystallizes from water in needles with a yellow-orange color.

0.6613 g substance: loss in weight upon drying (125°) 0.0742 g.
0.6487 g dry substance: 0.1647 g Na₂SO₄.
Found %: H₂O 11.22; Na 8.22.
C₁₀H₆O₅NSNa·2H₂O. Calculated %: H₂O 11.57.
C₁₀H₆O₅NSNa. Calculated %: Na 8.36.

The substance dissolves very slowly in aqueous sodium bisulfite; from the solutions the bisulfite compound of the nitrosonaphtholsulfonic acid can be isolated.

1-Nitroso-2,4-dihydroxynaphthalene. To a solution of 2 g of the crystalline sodium salt of the nitroso compound in 50 ml of water, 9 ml of 10% caustic soda is added, and the liquid is heated for one hour on the water bath. Upon acidification with hydrochloric acid, sulfur dioxide is evolved, and a dark yellow precipitate of 1-nitroso-2,4-dihydroxynaphthalene is formed; yield 1.1 g. It crystallizes from alcohol in the form of yellow needles with m.p. 180°.

1-Phenylamino-1-nitroso-2-naphthol. To a solution of 2 g of the dry sodium salt of nitrosonaphthol-4-sulfonic acid in 50 ml of water, 40 ml of a 3.5% aqueous solution of aniline is added, and after 2 hours the orange precipitate is filtered off. Yield 1.82 g. After recrystallization from alcohol, the orange needles melted at 218°.

4-p-Tolylamino-1-nitroso-2-naphthol. This was prepared in a similar way with a 3% solution of p-toluidine. Yield 1.85 g. After crystallization from alcohol, the orange platelets had m.p. 197°.

SUMMARY

1. The removal of the diazo group from 1-diazo-2-naphthol-4-sulfonic acid by means of an alkaline solution of stannous oxide gives the sodium salt of

2-naphthol-4-sulfonic acid, which crystallizes both with one and with two molecules of water.

2. Under the action of nitrous acid, 2-naphthol-4-sulfonic acid gives 1-nitroso-2-naphthol-4-sulfonic acid.

3. The nitroso compound is characterized by the great mobility of the sulfonic acid group, and under the action of dilute alkali is transformed into 1-nitroso-2,4-dihydroxynaphthalene; with primary aromatic amines, it gives 4-arylamino-1-nitroso-2-naphthol.

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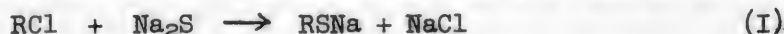
INVESTIGATIONS IN THE FIELD OF AROMATIC SULFIDE COMPOUNDS

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The K. E. Voroshilov Scientific-Research Institute of Organic Intermediates and Dyes

The present communication concerns several transformations of sulfide compounds of the benzene series, such as: thiophenols, mono- and disulfides, and in particular, polysulfides.

One of the most important reactions for the preparation of organic sulfide compounds is the replacement of halogen by sulfur, by means of the action of sulfides of the alkaline metals upon organic compounds with mobile halogen atoms [1]:



where n varies from 1 to 5 in different cases.

In the investigations of organic chemists, the question of the purity (individuality) of the mineral polysulfides used in these reactions is usually passed over in silence. We, however, consider it necessary to emphasize several conditions known to be essential for the success of the work.

When an excess of sulfur is dissolved in solutions of monosulfides of the alkaline metals (the usual, but unreliable method for the preparation of individual polysulfides) there is usually obtained, along with the desired polysulfide, a mixture of sulfides of different composition. All the alkaline metals form two stable compounds: one of them is invariably the disulfide, the other, for lithium and sodium, is the tetrasulfide, and for the remaining metals, the pentasulfide. A reliable method for the preparation of the indicated higher stable compounds is the solution of sulfur in alcoholic solutions of the sulfohydrates of the corresponding metals.

A method for the preparation of the polysulfide of the composition Na_2S_3 involves the heating for a brief period of a mixture of sodium and sulfur in toluene, [3].

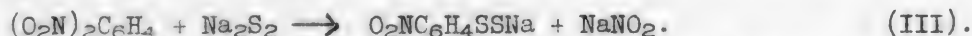
Several methods have been proposed for the analysis of the polysulfides [4]. After suitable investigation we decided that the only satisfactory method was that of Kurtenacker.

There is no uniformity of opinion in the literature with regard to the relation between the sulfur atoms themselves, either in organic or in mineral polysulfides. However, in organic disulfides, the "chain" bond ($-\text{S}-\text{S}-$) of the sulfur atoms is very well shown by their chemical reactions [5]. The Raman spectra [6] of organic disulfides, as well as of sulfur monochloride, are evidence in favor of such bonds. The "chain" structure of S_2Cl_2 is confirmed by investigations in the field of electronic diffraction [7].

As Blanksma [8] has shown, the action of sodium disulfide upon compounds

which contain halogen in a position ortho or para to a nitro group gives disulfides; o-dinitrobenzene reacts in exactly the same way. Sodium trisulfide and tetrasulfide behave similarly, according to Blanksma's opinion, to give, for example, with o-dinitrobenzene, 2,2'-dinitrodiphenyl trisulfide and tetrasulfide [9].

Blanksma also obtained 2,2'-dinitrodiphenyl tetrasulfide by oxidizing o-nitrophenyl thiomercaptide with iodine; this was formed in accordance with his assumption, according to equation (III):

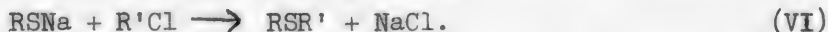


On the basis of his work, Blanksma considered that he had demonstrated the "linear" arrangement of the atoms of sulfur in organic and mineral polysulfides; for example, a diaryl tetrasulfide has the structure R-S-S-S-S-R [10].

We must note that the 2,2'-dinitrodiphenyl trisulfide of Blanksma was not confirmed by later investigations [11]. We also, despite all our efforts, did not succeed in obtaining the tetrasulfide either from o-dinitrobenzene or from p-bromonitrobenzene by the reaction of 2 molecules of the nitro compounds with 1 molecule of Na_2S_4 . Equally unsuccessful were our attempts to synthesize the tetrasulfide by the second method recommended by Blanksma:



In all cases, we invariably obtained a mixture of sulfur with almost pure diaryl disulfide. It is scarcely possible to doubt that in the two-phase method organic monosulfides are formed by the action of sodium sulfide on halogen-nitro compounds:



This course of the reaction is shown by the formation, according to mechanism (VI), of mixed monosulfides in almost quantitative yields [12]. According to Blanksma, the same mechanism holds for the formation of polysulfides; this is expressed for disulfides in equations (VII) and (VIII):



However, because of the lack of confirmation of the formation by this method of tri- and tetrasulfides, as we have mentioned above, we cannot exclude the possibility that disulfides are formed in other ways, for example, by the oxidation of the mercaptides formed as intermediates, either by the oxygen of the air or by nitro groups.

In order to decide this question, we synthesized several disulfides both by the usual one-phase method, starting with two molecules of nitro compounds and 1 molecule of Na_2S_2 , and by the two-phase method, according to equations (VII) and (VIII), and we obtained the corresponding disulfides in uniformly good yields.

For the sake of complete clarity, we had yet to synthesize mixed disulfides by the two-phase method; for purposes of comparison, we intended to obtain the same compounds by the known method (IX) [13]:



By varying a number of components, however, we convinced ourselves that instead of the expected mixed disulfides we were obtaining mixtures of two simple disulfides. In order to explain the rules of formation we had found, we assumed that the mixed disulfides, as they were formed, were subjected to some sort of reaction by the active components of the mixture, and in the first place, by the thiomercaptides, which are completely unknown, and apparently very unstable compounds.

In order to make what was happening entirely clear, we projected the following plan: first of all, to confirm the actual presence of thiomercaptides; then, before considering the reaction between the mixed disulfides and thiomercaptides, and also apparently, the inevitable reaction with mercaptides, to break down into simple steps the reaction of disulfides with Na_2S_2 and Na_2S ; and finally, to consider the reaction of the mixed disulfides with mercaptides and thiomercaptides.

This is the sequence in which our remaining material is arranged.

Thiomercaptides

We could assume that the thiomercaptides, NS_2Na , would resemble in their properties the well known mercaptides, and would, in the first place, possess the ability to act as reducing agents, and therefore, to be easily oxidized.

If alcoholic solutions of silver nitrate or lead acetate are added to an alcoholic solution of p-nitrophenyl thiomercaptide, a precipitate quickly forms. In the former case it is pale yellow, in the second, clear orange. It very quickly turns black in the air, decomposing to give silver sulfide or lead sulfide plus an organic disulfide. The sodium and potassium salts of nitrophenyl thiomercaptide are very soluble in water and alcohol, and easily oxidize in the air to give the disulfides and sulfur. When not in contact with air, they decompose much more slowly, to give other compounds: mercaptides and sulfur. The second reaction takes place much more quickly in concentrated solutions. Below are given the results of experiments with spontaneously decomposing p-nitrophenyl thiomercaptide (3.1 g), which had stood for one day in a solution of alcohol (50 ml) at room temperature without the access of air and light. At the end of a day, a precipitate of sulfur formed. The reaction mixture was filtered with the exclusion of air; the precipitate was soluble in carbon disulfide, and was almost pure sulfur. The solution contained mercaptide, whose quantity (according to analysis with iodine) amounted to about 99% of the theoretical. Upon oxidation with iodine, this solution gave a quantitative precipitate of pure 4,4'-dinitrodiphenyldisulfide. p-Nitrophenyl mercaptide was also determined in the form of 2,2',4'-trinitrodiphenyl sulfide; for this determination, an alcoholic solution of dinitrochlorobenzene was added to our mercaptide solution. The amount of mixed sulfide amounted to 96.5% of that calculated by the iodine method.

On the basis of what has been presented, we cannot doubt the existence of thiomercaptides.

The Action of Na_2S and Na_2S_2 on Aromatic Disulfides

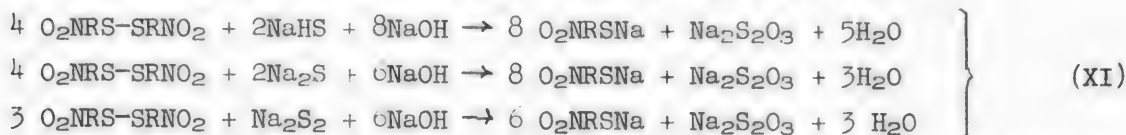
Despite the considerable importance of mercaptans for synthetic purposes, these reactions are not correctly explained in the literature.

Up to the present time [14], the equation of Otto [15] is the one usually given:



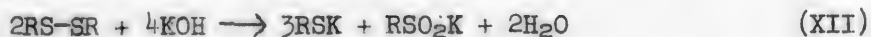
We cannot agree that it is correct, as we know that for the cleavage of the disulfide a single molecule of sodium sulfide is actually sufficient.

The mechanism of K. Brand [16] has still less in its favor:

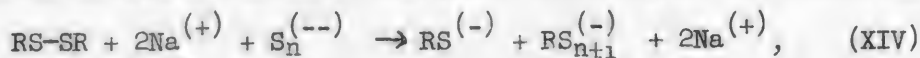


as here two different reactions are joined together - the reaction of metallic sulfides and of caustic alkalies on disulfides. And it is well known that with

the latter reagent there are obtained, along with mercaptides, sulfinic [17] or sulfenic [18] acids:

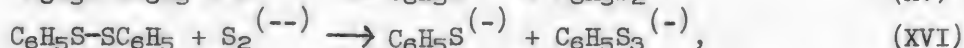
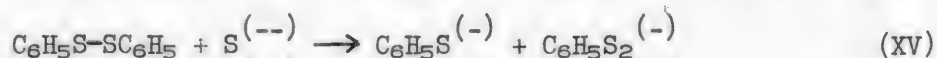


We assumed that the reaction of aromatic disulfides with solutions of metal sulfides in alcohol or in aqueous alcohol took place according to the following scheme:



i.e., with Na_2S , the final products would be mercaptide (1 molecule) and the thio-mercaptide RS_2Na (1 molecule); with Na_2S_2 , mercaptide (1 molecule) and the dithio-mercaptide RS_3Na (1 molecule).

In order to demonstrate the correctness of this assumption, we began with the simplest and most favorable example, taking Na_2S and diphenyldisulfide, in which there are no nitro groups to serve as a source of confusion because of reduction. Upon mixing equivalent amounts of these reagents with alcoholic solutions, there took place the evolution of heat and a sharp intensification of color; after 15 minutes, no sodium sulfide was left. The solution was acidified with dilute hydrochloric acid and shaken repeatedly with a large quantity of ether in an atmosphere of nitrogen. The aqueous-alcoholic layer used up no iodine, but the consumption of iodine by the ethereal layer equaled 93% of theory, basing the calculation on the Na_2S taken. The product in the ether was a mixture of diphenyl disulfide and diphenyl tetrasulfide. As is clear, the preliminary results do not contradict the assumption of our mechanism (XIV). However, we were convinced that the determination of the amount of diphenyl tetrasulfide in the mixture would be difficult; in addition, we were faced with the task of analyzing by this method a still more complicated mixture, in which, along with the disulfide, there might be a diphenyl hexasulfide - a compound whose existence was unconfirmed. In consideration of all this, we decided to risk taking another path, which at first glance was still less promising. We attempted to determine quantitatively the compounds obtained by the reaction of 1,2,4-chlorodinitrobenzene on mixtures of the cleavage products of diphenyl disulfide by sodium sulfide and disulfide. If the latter reaction, in accordance with our assumptions, is expressed by equations (XV) and (XVI):



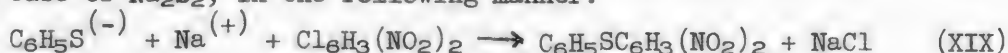
then the formation of reaction products with chlorodinitrobenzene for the case of Na_2S is shown by equations (XVII) and (XVIII):



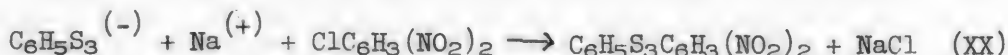
and



and for the case of Na_2S_2 , in the following manner:



and

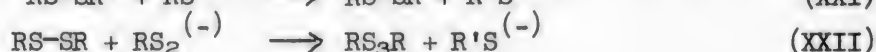
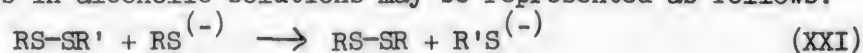


It appeared, however, that the actual results of this treatment of the reaction mixture with chlorodinitrobenzene had nothing in common with these assumptions. We present them in the form of Table 1.

TABLE 1

Final compound	Cleavage of diphenyldisulfide (in %)	
	by sodium sulfate	by sodium disulfite
Diphenylsulfide	73.8	73.3
Tetranitrodiphenyldisulfide	10.0	79.9
Tetranitrodiphenylsulfide.....	55.2	4.3
2,4-Dinitrodiphenylsulfide.....	29.9	20.6
Chlorodinitrobenzene.....	5.9	-
Total From diphenyldisulfide....	103.7	93.9
From chlorodinitrobenzene	101.0	104.8

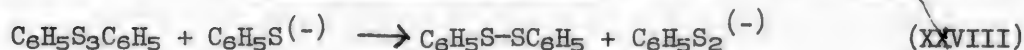
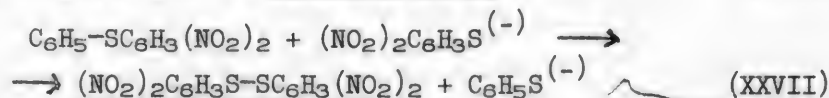
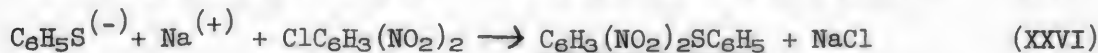
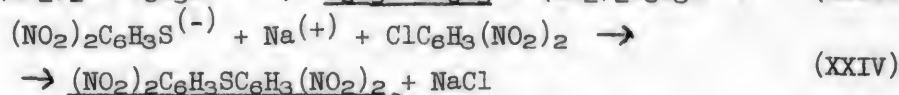
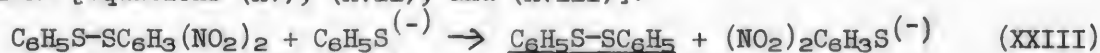
Because of the proper choice of starting materials, we were able to analyze the products of reaction in complicated mixtures. Tetranitrodiphenyldisulfide and tetranitrodiphenyl sulfide precipitate practically completely from alcoholic solutions; they are separated by means of acetone. Having determined in advance that 2,4-dinitrodiphenyl sulfide and diphenyl disulfide remained in solution, we devised a method for separating them with Na_2S ; this converted the diphenyl disulfide into mercaptide, which went into solution, from which the diphenyl disulfide was once more regenerated by careful oxidation with potassium ferricyanide. In the mother liquors (the principal ones) there was very little chlorodinitrobenzene. It is very important that no significant amount of sulfur was observed. To some extent the striking difference between the suggested and the actual course of the reaction can be explained by the reducing action of the mercaptides on the mixed disulfides and trisulfides. For convenience in presenting this question, we shall consider it separately; meanwhile, assuming that such reactions are actually taking place, we shall draw the necessary conclusions. Comparing the mercaptides and thiomercaptides to sodium sulfide and disulfide, we see that their reactions with the mixed disulfides in alcoholic solutions may be represented as follows:



or

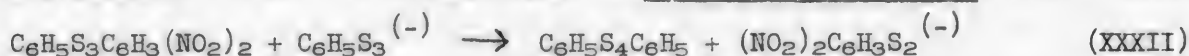
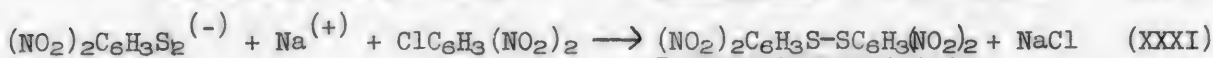
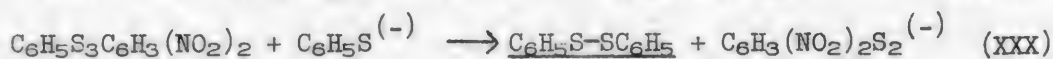
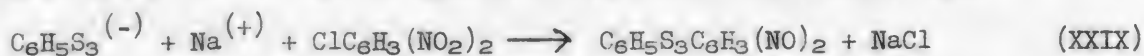


Taking into account the cleavage of the diphenyl disulfide by sodium sulfide, and the subsequent treatment of the mixture of products with chlorodinitrobenzene [equations (XV), (XVII), and (XVIII)]:



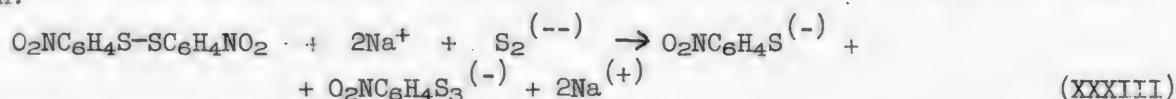
etc.

It can be seen that the more complicated a compound is, the less probable is its formation, and in particular the less probable its continued existence in so complicated a situation. The more stable compounds have been underlined; they correspond precisely to those compounds which are formed in the reaction mixture. It is clear, also, that the amounts of these compounds are determined both by the velocities of reduction of the corresponding intermediate compounds, and by the velocities of their coupling with chlorodinitrobenzene. There is an obvious sharp quantitative difference in the results with Na_2S and with Na_2S_2 (cf. Table 1). In the second case, an important role must be played by the following reaction, which is almost absent in the case of Na_2S [see equations (XVI), (XIX), (XX)]:



etc. Here, therefore, one of the most important compounds that we would expect is tetranitrodiphenyl disulfide and this expectation is accurately confirmed by experiment. Very significant is the absence of sulfur among the products of reaction; this indicates the relative stability of the sulfur-rich intermediate products, whose spontaneous decomposition obviously takes place much more slowly than their further transformation into the more stable final compounds.

In order to demonstrate the general character of the cleavage of disulfides by alkaline sulfides, let us also consider the reaction of 2,2'-dinitrodiphenyl disulfide with Na_2S and Na_2S_2 . At the beginning, to our surprise, we were forced to note the almost completely uniform results in the two cases: along with large amounts of 2,2'-dinitrodiphenyl disulfide and 2,4,2',4'-tetranitrodiphenyl sulfide, there was a small amount of 2,2',4'-trinitrodiphenyl sulfide; in the experiment with Na_2S_2 , the expected tetranitrodiphenyl disulfide was entirely absent. The cause of this, apparently, was the instability in more concentrated solution of the o-nitrophenyl dithiomercaptide, obtained according to the equation:



In addition, when we went over to more dilute solutions (approximately 0.004 M), the results were very close to those which were observed in the reaction of diphenyl disulfide with alkaline sulfides. Below are listed the experiments on the cleavage of 2,2'-dinitrodiphenyl disulfide by sodium sulfide and disulfide, with subsequent treatment of the reaction mixture by chlorodinitrobenzene (Table 2).

Thus, the hypotheses we have made, among them the original one concerning the course of the reaction between aromatic disulfides and metallic sulfides may be considered correct. Let us pass on to the next section of our work, in which we hope to examine with still greater completeness and reliability the questions considered above.

The Preparation of Mixed Disulfides and 2,2'-Dinitrodiphenyl Trisulfides and The Reaction of These Compounds with Mercaptides

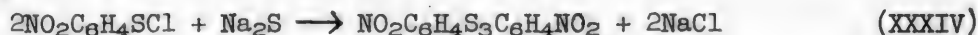
As has already been indicated, mixed disulfides may be obtained according to equation (X). Starting with o-nitrophenyl thiochloride and thiophenol in

TABLE 2

Final compound	cleavage of 2,2'-dinitrodiphenyldisulfide (%)	
	Na ₂ S	Na ₂ S ₂
2,2'-Dinitrodiphenyl disulfide...	77.6	78.6
Tetranitrodiphenyl disulfide.....	—	83.4
Tetranitrodiphenyl sulfide	75.0	—
2,4,2'-Trinitrodiphenyl sulfide .	18.3	9.0
Total From chlorodinitrobenzene	93.3	92.4
From 2,2'-dinitrodiphenyl disulfide	95.9	87.6

ethereal solutions, we prepared o-nitrodiphenyl disulfide with a yield of 96% of theory [19]. In exactly the same way, we obtained from 2-nitrophenyl thiochloride and p-nitrothiophenol a substance with m.p. 159-160°; starting with 2,4-dinitrothiophenol as our second reagent, we obtained 2,2',4'-trinitrophenyl disulfide, with m.p. 175-176°. In both cases, the yield amounted to 91-92% of theory. In their properties, the mixed disulfides resembled the symmetrical ones, but were less stable, for example, to alkalis and reducing agents.

2,2'-Dinitrodiphenyl trisulfide was less easy to obtain. We decided not to try to obtain it by the action of o-nitrothiophenol on o-nitrophenyl dithiochloride [11], as the sulfur monochloride necessary for the preparation of the dithiochloride is very unstable, and always contains sulfur chlorides which may alter the results. We succeeded in solving the problem according to the following equation:



The secret of our success was the complete absence of water or alcohol. If we take, for example even a very minute amount of alcohol to dissolve the Na₂S, instead of the trisulfide, the 2,2'-dinitrodiphenyl disulfide is obtained. Positive results are obtained in ether, and still better, in chloroform. To sodium sulfide which has been finely powdered (under benzene) there is added a solution of thiochloride in ether; the particles of Na₂S become covered with a brick-red film, obviously o-nitrophenyl thiomercaptide, and at the same time, as the solution is shaken, a precipitate of NaCl forms. Thus the step-by-step course of the reaction may be observed. The 2,2'-dinitrodiphenyl trisulfide is in the form of yellow crystals, melting at 172-174°. The yield reached 50% of theory.

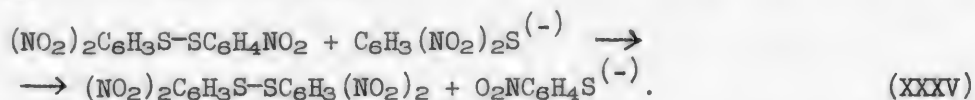
The question of the possibility of reaction between disulfides and mercaptides arose at the time of the fruitless attempts to obtain 2,4'-dinitrodiphenyl disulfide according to equations (VII) and (VIII), starting with p-nitrophenyl thiomercaptide and o-dinitrobenzene. The cause for our failure to obtain this disulfide might have been its instability under the action, in the first place, of p-nitrophenyl thiomercaptide. We prepared the latter compound in the usual way, by the reaction of Na₂S₂ with p-bromonitrobenzene in alcohol and the addition of 2,4'-dinitrodiphenyl disulfide. The results were not clear. Along with large quantities of difficultly separable compounds, we succeeded in observing a small amount (12 to 25%) of 2,2'-dinitrodiphenyl disulfide. Starting with p-nitrophenyl mercaptide instead of p-nitrophenyl thiomercaptide, the former being easy to prepare in pure form, we confirmed the fact that there was no reaction with 2,4'-dinitrodiphenyl disulfide.

Our attempts to obtain 2,2'-dinitrodiphenyl trisulfide by the method of Blanksma, from o-dinitrobenzene and sodium trisulfide with the guaranteed composition Na₂S₃, were completely unsuccessful.

In the literature we found a single direct reference to the possibility of cleavage of a mixed disulfide by mercaptide. Using thiophenol in ether solution to act on o-nitrophenyl thiochloride, Lecher obtained a quantitative yield of o-nitrophenyl disulfide. When instead of thiophenol he used its sodium salt in alcoholic solution, he obtained 2,2'-dinitrodiphenyl disulfide and diphenyl disulfide, *i.e.*, two simple disulfides [20]. Later, Malisoff [21] discussing this work, expressed doubt as to whether the mercaptides, in general, were capable of such reactions.

We repeated the experiment of Lecher, but instead of an alcoholic solution of the thiophenolate we used the dry thiophenolate in absolute ether to react with o-nitrophenyl thiochloride; we thus obtained o-nitrodiphenyl disulfide smoothly. Upon replacing the ether with alcohol, we obtained a mixture of the two simple disulfides. It is clear from this that only when the mercaptides are in an ionized state are they capable of reducing disulfides. It also became clear that in order to decide the question concerning the possibility of reaction between disulfides and mercaptides, it is necessary in each separate case to resort to experiment.

The different cases of reactions between mixed disulfides and mercaptides and thiomercaptides are given in two tables (3 and 4) in the experimental part of our work. As is obvious (Table 3), all the mercaptides investigated, with the exception of p-nitrophenyl mercaptide, cleave the mixed disulfides. In the two final experiments, instead of one simple disulfide, two were obtained, as the alkaline solutions contained the two corresponding mercaptides. This is understandable from the fact that only at the very beginning of the reaction does the original mercaptide take part in the reaction exclusively, reacting with the disulfide according to the equation (XXXV):



Later, the second mercaptide also takes part in the reaction, so that the final ratio of products of the reaction is directly dependent upon the velocity of cleavage of the mixed disulfide by both these reducing agents. In particular, it is possible to confirm the fact that o-nitrophenyl mercaptide is much more active than 2,4-dinitrophenyl mercaptide (cf expts. 2 and 4).

In their reducing action, the thiomercaptides resemble the mercaptides (table 4). Here too, 2,4-dinitrophenyl thiomercaptide gives a mixture of disulfides. Under exactly the same conditions, p-nitrophenyl thiomercaptide shows little activity. In connection with this fact, we returned to our experiments on the preparation of 2,4'-dinitrodiphenyl disulfide in two phases by the action of o-dinitrobenzene on p-nitrophenyl thiomercaptide (from p-bromonitrobenzene and Na_2S_2). Carrying out the entire reaction at room temperature in order to diminish the reducing action of the thiomercaptides, we obtained more than 35% of the theoretical amount of mixed disulfide, a large quantity of this compound remaining in the unseparated mixtures.

In conclusion, we have yet to investigate the behavior of aromatic trisulfides in our reactions. There can be no doubt that the mixed trisulfides, as they are formed, either are transformed into disulfides, losing an atom of sulfur, or, as is more probable, are cleaved, for example, according to equation (XXX).

It is more difficult to decide in advance the fate of the simple trisulfides. As an example, we took 2,2'-dinitrodiphenyl trisulfide and subjected it to the action of Na_2S , of thiophenolate, and of 2,4-dinitrophenyl mercaptide. In the first experiment, the reaction mixture was treated, as usual, with chlorodinitrobenzene. Two substances were obtained, tetranitrodiphenyl disulfide, and 2,2'-di-

nitrodiphenyl disulfide. In the second experiment we obtained diphenyl disulfide and o-nitrophenyl mercaptide. Thus, there is no doubt about the reduction cleavage of the trisulfide in these two cases. Completely different results are obtained with 2,4-dinitrophenyl mercaptide. After standing for a day, the reaction mixture almost quantitatively forms 2,2'-dinitrodiphenyl disulfide. The cause of the loss of sulfur by the trisulfide is apparently the alkalinity of the medium, which favors the dissociation of the mercaptide. To confirm this, we did the following: to a suspension of the trisulfide in methyl alcohol, we added an alcoholic solution of o-nitrophenolate. After 12 hours, we observed that the trisulfide was almost quantitatively converted into 2,2'-dinitrodiphenyldisulfide.

As has been noted, according to Blanksma, dinitrodiphenyl trisulfide and tetrasulfide can be obtained by the action on the corresponding halogen nitro compounds of Na_2S_3 and Na_2S_4 . In connection merely with the demonstrated loss of sulfur by dinitrodiphenyl trisulfide in the presence of even very weak alkali, the fact that Blanksma was mistaken can hardly be in doubt.

EXPERIMENTAL

Preparation of Sodium Sulfohydrate, Sodium Sulfide, and Sodium Polysulfides

Pure caustic soda (8 to 10 g) is dissolved in absolute methyl alcohol (200 ml) and the liquid is divided into two equal parts. In order to obtain the sulfohydrate, half of the solution is saturated with hydrogen sulfide until the disappearance of the action on phenolphthalein; the small excess of hydrogen is removed by a weak current of nitrogen. In order to prepare a solution of sodium sulfide, the sulfohydrate solution is mixed with the second half of the alcoholic alkali.

By dissolving the calculated quantity of pure sulfur with moderate heating (60°) in the alcoholic solution of sodium sulfide, the disulfide is obtained.

The tetrasulfide is prepared by dissolving sulfur in an alcoholic solution of sodium sulfohydrate with gentle heating (45°); the amounts of reagents are calculated from the equation:



Sodium trisulfide, because of its instability, is prepared directly before use: to metallic sodium (1 g) in boiling toluene (50 ml) a toluene solution of sulfur (2.2 g in 100 ml) is added. After boiling for 15 minutes, the solution is cooled and filtered, the precipitate washed with hot toluene, and the solvent evaporated off in a vacuum dessicator. All the manipulations with the solutions of alkali sulfide, including storage, are carried out in an atmosphere of nitrogen. Under these conditions, they keep for 8-10 days without change in titre.

All the solutions of alkali sulfide that were prepared were analyzed. The total iodine number was determined in the usual way, by oxidation of the sulfide in question with an excess of iodine; the thiosulfate was determined by difference after precipitating all the alkaline sulfide from the solution with zinc acetate. Polysulfide sulfur was determined by the method of Kurtenacker [4], which was based on the reaction:



A definite volume of polysulfide solution (25 ml) was mixed with a 10% solution of sodium sulfite (25 ml) at 50° . After 20 minutes, the Na_2S was precipitated with a solution of zinc acetate, the precipitate filtered on a dry filter, and a definite volume of the liquid titrated with iodine after the excess of Na_2SO_3 had been bound by formalin.

The Action of Sodium Tetrasulfide on o-Dinitrobenzene

An alcoholic solution of tetrasulfide (0.87 g - 0.005 g-mol in 10 ml) was added drop by drop to an alcoholic solution of o-dinitrobenzene (1.68 g - 0.01 g-mol in 50 ml) at 0°. After 1.5 hours, the precipitate was filtered and washed with alcohol. The product obtained melted over a wide range; after repeated treatment with carbon disulfide, pure 2,2'-dinitrodiphenyl disulfide (0.9 g) remained; upon evaporation of the carbon disulfide, almost pure sulfur (0.5 g) was obtained.

The Oxidation of o-Nitrophenyl Thiomercaptide with Iodine

An alcoholic solution of sodium disulfide (0.55 g - 0.005 g mol in 10 ml) was added drop by drop to an alcoholic solution of o-dinitrobenzene (0.84 g - 0.005 g-mol in 50 ml); the reaction temperature was 5°. After 30 minutes, the solution was oxidized with a solution of iodine in alcohol. The dark violet color changed into a pale yellow one, and a voluminous precipitate (0.8 g) formed; this had a very extended melting range, from 145 to 172°. After repeated treatment with carbon disulfide and a single crystallization from acetone, pure 2,2'-dinitrodiphenyl disulfide with m.p. 195-196° was obtained. The carbon disulfide solution contained some impure sulfur. Thus, Blanksma's tetrasulfide was not observed.

The Preparation of 2,2'-Dinitrodiphenyl Disulfide

a) In one phase. To an alcoholic solution of o-dinitrobenzene (4.2 g in 170 ml) there was added an alcoholic solution of sodium disulfide (1.38 g in 30 ml) at 25°. The molar ratio of the reagents was 2:1. After 30 minutes, the precipitate was filtered off, washed with alcohol and water, and dried. The substance (3.1 g) melted in the interval 184-188°. After treatment with carbon disulfide, pure 2,2'-dinitrodiphenyl disulfide (2.9 g), with m.p. 194-195.5°, remained.

b) In two phases. To o-dinitrobenzene (3.36 g - 0.02 mol.) in 100 ml alcohol there was added with good cooling an alcoholic solution of sodium disulfide (2.2 g - 0.02 g mol in 43 ml). After 6 minutes, no disulfide remained. In order to introduce the second phase into the reaction mixture, 3.36 g of o-dinitrobenzene in 50 ml of alcohol was added at 40°; after an hour, the solution was filtered. The usual treatment with carbon disulfide gave 4.94 g of pure 2,2'-dinitrodiphenyl disulfide; upon evaporation of the carbon disulfide, a small amount of sulfur (0.04 g) was obtained. To recover the remainder from the filtrate the alcohol was evaporated off and the residue treated with live steam to remove the remaining o-dinitrobenzene (0.12 g) and o-nitroaniline (0.43 g). Taking into account the 2,2'-dinitrodiphenyl disulfide in the alcoholic solution (0.28 g), the total quantity of all the substances determined amounted to 94.2% of theory, basing the calculation on the o-dinitrobenzene.

Preparation of 2,4,2',4'-Tetranitrodiphenyl Disulfide (In Two Phases)

To an alcoholic solution of 2,4-chlorodinitrobenzene (2.025 g - 0.01 g-mol in 50 ml) sodium disulfide (1.1 g - 0.01 g-mol) in alcohol (13 ml) was added. The temperature did not exceed 20°. After 5 or 6 minutes the reaction was complete. A second portion of chlorodinitrobenzene was added and allowed to stand until the following day. The 2,4,2',4'-tetranitrodiphenyl disulfide (3.5 g) obtained was purified by treatment with carbon disulfide. The compound decomposed above 280°, but did not melt. Yield 86% of theory.

3.058 mg substance: 4.086 mg CO₂; 0.418 mg H₂O.

2.992 mg substance: 0.381 ml N₂; (21°, 743 mm).

Found %: C 36.44; H 1.53; N 14.24.

C₁₂H₆N₄O₈S₂. Calculated %: C 36.2; H 1.55; N 14.1.

Reaction of o-Nitrophenyl Thiomercaptide with 1,2,4-Chlorodinitrobenzene

A solution of 3.4 g of o-dinitrobenzene in 70 ml of alcohol was mixed at 10° with a solution of Na₂S₂ (2.2 g - 0.02 g-mol in 26 ml). After 5 minutes, an alcoholic solution of chlorodinitrobenzene (4.1 g in 40 ml.) was added. On the following day, the precipitate was filtered off, washed, dried, and subjected to the usual treatment with carbon disulfide. The substance (4.1 g) melted with difficulty; it was extracted by repeatedly boiling with acetone. The residue (3.0 g) was 2,4,2',4'-tetranitrodiphenyl disulfide.

4.000 mg substance: 5.368 mg CO₂; 0.507 mg H₂O.

3.162 mg substance: 0.404 ml N₂ (21°, 744 mm).

Found %: C 36.6; H 1.42; N 14.29.

C₁₂H₆N₄O₈S₂. Calculated %: C 36.2; H 1.55; N 14.1.

From the acetone, 1.10 g of 2,2'-dinitrodiphenyl disulfide was isolated. No mixed disulfide was observed.

Reaction of p-Nitrophenyl Thiomercaptide with 2,4-Chlorodinitrobenzene

A solution of 4.04 g (0.02 g-mol) of p-bromonitrobenzene in 70 ml of alcohol was mixed at 45° with 2.2 g of sodium disulfide (0.02 g-mol) in 26 ml of alcohol. After 100 minutes, the preparation of the thiomercaptide was complete. Chlorodinitrobenzene (4.1 g) in 40 ml of alcohol was added at 45°, and the mixture maintained at this temperature for about an hour. After treatment similar to what has already been described, 2.8 g of the tetranitrodiphenyl disulfide and about 1.0 g of 4,4'-dinitrodiphenyl disulfide were obtained.

The Spontaneous Decomposition of p-Nitrophenyl Thiomercaptide

p-Nitrophenyl thiomercaptide was obtained by the method described and allowed to stand for 3 days in a dark place. The precipitate was filtered out and washed with alcohol and water; it was almost pure sulfur (0.8 g). The aqueous-alcoholic solution was split into three parts and in one the total amount of mercaptide obtained (2.74 g) was determined iodometrically. The second part was oxidized with potassium ferricyanide and the amount of 4,4'-dinitrodiphenyl disulfide was determined. Finally, in the third part the mercaptide was estimated in the form of 2,2',4'-trinitrodiphenyl sulfide (5.47 g), obtained by the reaction with chlorodinitrobenzene.

A second experiment on the spontaneous decomposition of p-nitrophenyl thiomercaptide was carried out in the presence of 2.0 g of o-nitroanisole. The results of both experiments were identical. No reduction products of o-nitroanisole were found.

The Synthesis of Several Initial Products

o-Nitrophenyl Thiochloride. 2,2'-Dinitrodiphenyl disulfide (20 g) was suspended in 100 ml of carbon tetrachloride and chlorine was passed in until the precipitate completely dissolved (from 1.5 to 3 hours). The thiochloride precipitated out in the form of yellow needles; to complete the crystallization, the solution was cooled with ice. The product (13 or 14 g) did not need purification (m.p. 75°).

p-Nitrophenyl Mercaptan, o-Nitrophenyl Mercaptan, and 2,4-Dinitrophenyl Mercaptan. To a hot solution of 10.5 g of p-bromonitrobenzene in 100 ml of alcohol, there was gradually added an alcoholic solution of sodium sulfide (4 g in 50 ml). After 20 minutes, the solution was diluted with 250 ml of water and filtered into 50 ml of a solution of 17% hydrochloric acid. The solution was cooled to 0° and the mercaptan filtered, washed well with water, squeezed out thoroughly, and dried in a vacuum dessicator. For purposes of purification, it could be reprecipitated. Yield 50% of theory. M.p. 75°. It was analyzed before use. In order to obtain

o-nitrophenyl mercaptan, the reagents were mixed at 40°, and the rest of the procedure carried out as above. Yield, 25 to 30% of theory.

The preparation of 2,4-dinitrophenyl mercaptan could be carried out at a lower temperature (25°). Yield about 90% of theory, m.p. 131°.

Diphenyl Disulfide. Thiophenol (22.2 g - 0.2 g mol) was dissolved in a 20% solution of caustic soda and oxidized while hot with 75 g of potassium ferricyanide in 120 ml of water. When the diphenyl disulfide solidified, it was filtered off and washed. The yield was almost quantitative. For purification, it was recrystallized from alcohol. M.p. 60-61°.

2,4'-Dinitrodiphenyl Disulfide. p-Nitrophenyl mercaptide (3.1 g) in 50 ml of ether was mixed with an ethereal solution of o-nitrophenyl thiochloride (3.8 g in 50 ml). The following day, the precipitate was filtered off and washed with ether. Yield 88% of theory; m.p. 156-157°. The substance was purified from a mixture of ether and chloroform. The melting point of the pure compound was 159.2-159.68mm. The melting point of the pure compound was 159.2-159.68mm.

4.340 mg substance: 7.441 mg CO₂; 0.920 mg H₂O.

3.753 mg substance: 0.313 ml N₂ (24°, 740 mm).

Found %: C 46.76; H 2.37; N 9.33.

C₁₂H₈N₂O₄S₂. Calculated %: C 46.75; H 2.6; N 9.08.

2,2',4'-Trinitrodiphenyl Disulfide. 2,4-Dinitrophenyl mercaptan (4.0 g - 0.02 g-mol.) was suspended in 80 ml of ether and an ethereal solution of o-nitrophenyl thiochloride (3.8 g - 0.02 g mol in 50 ml) was added; the mixture was shaken for 1 hour at room temperature. The yield of pure compound was about 80% of theory. M.p. 175-176°.

3.491 mg substance: 5.409 mg CO₂; 0.650 mg H₂O.

3.214 mg substance: 0.349 ml N₂ (23°, 728 mm).

Found %: C 40.7; H 2.08; N 12.0.

C₁₂H₇N₃O₆S₂. Calculated %: C 40.8; H 1.98; N 11.9.

o-Nitrodiphenyl Disulfide was obtained from thiophenol and o-nitrophenyl thiochloride in the dry form. Upon evaporation of the ether, there remained almost the calculated amount of the compound. The product, recrystallized from alcohol, melted at 53-54°, the completely pure compound at 55°.

2,2'-Dinitrodiphenyl Trisulfide. Sodium sulfide (0.78 g - 0.01 g-mol) finely powdered under benzene or chloroform, was introduced into a solution of o-nitrophenyl thiochloride (3.8 g - 0.02 g-mol) in 50 ml of chloroform at room temperature. The reaction took place with a slight evolution of heat. After 15 minutes, the precipitate was filtered off, washed with ether, water, alcohol, and again with ether. The compound melted at 172-174°. The main part of the filtrate in chloroform was diluted with ether; upon cooling with ice, a second fraction, of less pure material (m.p. 168-171°) was separated out. The total yield was about 50% of theory. The compound was unchanged after treatment with carbon disulfide.

The Reduction Cleavage of Disulfides by Alkaline Sulfides. Diphenyl Disulfide and Sodium Sulfide. To an alcoholic solution of diphenyl disulfide (2.18 g - 0.01 g-mol in 50 ml) there was added a solution of sodium sulfide (0.78 g - 0.01 g-mol) in alcohol (20 ml) at room temperature. The solution immediately took on an orange color; after 15 minutes, the Na₂S was used up. After 15 to 20 minutes more, an alcoholic solution of 2,4-chlorodinitrobenzene (4.05 g - 0.02 g-mol in 40 ml) was added. The color of the reaction mixture first deepened, then quickly grew lighter. The following day, the precipitate was filtered off, washed with alcohol and water, and dried. A mixture of substances was obtained (2.50 g), with

a wide melting range. After repeated treatment with alkali in hot acetone, part of the substance (0.30 g) remained undissolved; a small amount of it (0.10 g) crystallized out immediately upon cooling of the acetone. This was tetranitrodiphenyl disulfide. Upon removal of the acetone by evaporation, 2,4,2',4'-tetranitrodiphenyl sulfide was removed in portions (1.2 g with m.p. 196-197° and 0.83 g with m.p. 193-195°). The solvent was driven off completely from the alcoholic filtrate; the residue (3.50 g) was an easily liquefied substance. A sample of it (1.00 g) was suspended in alcohol (5 ml), diluted with water (10 ml), and shaken for 2 hours at 10° with an alcoholic solution of sodium sulfide (0.2 g in 4 ml). It was then filtered and washed with 5 ml of aqueous alcohol. In the precipitate, 2,4-dinitrodiphenyl sulfide (0.47 g) was obtained as a pure compound (m.p. 119.5-120.5°) after a single crystallization. The filtrate was heated to 60° and oxidized with an aqueous solution of potassium ferricyanide (1 g in 10 ml). It was cooled to 0°, and the precipitate filtered off and recrystallized from alcohol to give the pure diphenyl disulfide (m.p. 59-61°). A small amount of chlorodinitrobenzene (0.24 g) was found by determining the Cl⁻ after oxidation.

Diphenyl Disulfide and Sodium Disulfide

Alcoholic solutions of diphenyl disulfide (2.18 g ~ 0.01 g-mol in 50 ml) and sodium disulfide (1.10 g ~ 0.01 g-mol in 20 ml) were mixed at 15°. After 2 hours, an alcoholic solution of chlorodinitrobenzene was added, and the rest of the treatment was carried out exactly as above. The following compounds were obtained: tetranitrodiphenyl disulfide (3.18 g), tetranitrodiphenyl sulfide (0.136 g), 2,4-dinitrodiphenyl sulfide (1.14 g) and diphenyl disulfide (1.60 g).

2,2'-Dinitrodiphenyl Disulfide (in Suspension) and Sodium Sulfide

To a suspension of 2,2'-dinitrodiphenyl disulfide (1.54 g ~ 0.005 g-mol) in 50 ml of alcohol there was added at 0° an alcoholic solution of sodium sulfide (0.39 ~ 0.005 g-mol in 10 ml). After 2.5 hours, the suspension of disulfide dissolved. A solution of chlorodinitrobenzene (2.02 g ~ 0.01 g-mol in 20 ml) was added, and the mixture allowed to stand until the following day. The product which separated out (2.9 g) melted at 164-175°.

Upon treatment with carbon disulfide, the amount of product and the melting point remained unchanged. But continually repeated crystallization from acetone here permitted us to obtain in pure form 2,2'-dinitrodiphenyl disulfide (0.85 g) and 2,4,2',4'-tetranitrodiphenyl sulfide (0.6 g) with m.p. 196-197°. Approximately the same quantities of these products were obtained in less pure condition. In the main portion of the alcoholic filtrate, we found 2,2',4'-trinitrodiphenyl sulfide (0.2 g) with m.p. 132-133° (pure compound). Adding together the products of the same kind obtained at stages of crystallization of the different fractions, we obtain the following total:

2,2'-dinitrodiphenyl disulfide	1.19 g,
2,4,2',4'-tetranitrodiphenyl sulfide	1.37 g.
2,2',4'-trinitrodiphenyl sulfide	0.59 g.

2,2'-Dinitrodiphenyl Disulfide (in Suspension) and Sodium Disulfide

This experiment was carried out in the same way as has been described, replacing the sodium sulfide with the sodium disulfide (0.55 g in 6 ml of alcohol). After standing for 2.5 hours, the sodium disulfide was used up, but part of the compound was in the precipitate. Chlorodinitrobenzene was added, and the solution allowed to stand until the following day. The precipitate was filtered off as usual and treated with carbon disulfide; a large amount of sulfur (0.16 g) was found. The rest of the experiment was carried out the same way as the preceding experiment, with the following results:

2,2'-dinitrodiphenyl disulfide 1.15 g,
 2,4,2',4'-tetranitrodiphenyl disulfide 1.38 g,
 2,2',4-trinitrodiphenyl sulfide..... 0.60 g.

2,2'-Dinitrodiphenyl Disulfide (in Solution) and Sodium Disulfide

To a solution of the aromatic disulfide (0.154 g) in methyl alcohol (100 ml) at 0° there was added a solution of sodium disulfide (0.055 g in 3 ml). At the end of the reaction chlorodinitrobenzene in alcohol (0.204 g in 5 ml) was added. On the following day, as usual, the main quantity of the product (0.23 g) was separated; this consisted of tetranitrodiphenyl disulfide (0.15 g) and 2,2'-dinitrodiphenyl disulfide (0.046 g). After the alcohol had been removed from the main portion of the filtrate there remained a mixture of products (0.093 g) which melted over a wide temperature interval. Using alcohol and acetone, it was possible to isolate tetranitrodiphenyl disulfide (0.015 g) and 2,2'-dinitrodiphenyl disulfide (0.025 g). 2,2'-Trinitrodiphenyl sulfide was found to be present in the filtrates. Adding together the products of the same kind, we obtain the total:

2,4,2',4'-tetranitrodiphenyl disulfide 0.166 g,
 2,2'-dinitrodiphenyl disulfide 0.121 g,
 2,2',4-trinitrodiphenyl sulfide 0.029 g.

The Reduction Cleavage of Disulfides by Mercaptides and Thiomercaptides

Disulfides and Mercaptides. The results are given in Table 3. The different experiments were conducted under almost identical conditions; the treatment of the reaction mixtures was the same in all cases. To a suspension of the mixed disulfide in methyl alcohol (0.001 g-mol in 50 ml) there was added a solution of mercaptide (0.001 g-mol) in methyl alcohol (25 ml), obtained from the mercaptan and the calculated quantity of alcoholic alkali; the mixture was shaken for 1 hour at room temperature. The crystalline substance which separated out (precipitate 1) was filtered off, and washed with alcohol and water. The chief portion of the disulfide was here; it was the simple disulfide if an active mercaptide was used for the reaction (expts. 1 and 2) or the mixed disulfide (starting material) if the mercaptide used was not capable of causing cleavage (expt. 3), or, finally, a mixture of two simple disulfides (expts. 4 and 5) if both mercaptides, the original one and that formed in the very cleavage of the original mixed disulfide, were sufficiently active reducing agents. These substances separated out in almost pure form (expts. 1, 2, 3) or in the form of mixtures (expts. 3, 4) whose separation did not offer great difficulties, and has been previously described. After the removal of the precipitate (precipitate 1), the filtrate was diluted to twice the volume with water and after 2 or 3 hours, an additional small precipitate settled out (precipitate 2); this was an impure substance, which was not separated. Finally, the aqueous alcoholic filtrate after the removal of precipitate 2 contained mercaptides; part of this filtrate was used for the quantitative determination of mercaptides iodometrically, and another part was treated with potassium ferricyanide, which oxidized the mercaptan to disulfide, which could be easily isolated in pure form (expts. 1 and 2). We must note that in these experiments where mixtures of mercaptides were obtained (expts. 4 and 5) the latter were oxidized and identified in the form of disulfides. Thus, o-nitrophenyl mercaptide was determined in the form of 2,2'-dinitrodiphenyl disulfide (0.030 g; expt. 4) and 2,4-dinitrophenyl mercaptide in the form of tetranitrodiphenyl disulfide (0.194 g).

Disulfides and Thiomercaptides. Results are given in Table 4. p-Nitrophenyl thiomercaptide (expt. 1) is obtained by the reaction of p-bromonitrobenzene

TABLE 3

Expt. No.	Original compounds		Found	
	Mercaptide	Disulfide	Name of compound	Yield (in % of theory)
1	2-nitrophenyl-mercaptide	2,4'-dinitrodiphenyl sulfide	2,2'-dinitrodiphenyl disulfide Unseparated mixture 4-nitrophenyl mercaptide (pure disulfide form)	82.3 } 98.5 16.2 } 58.5
2	2-nitrophenyl-mercaptide	2,4,2'-trinitrodiphenyl sulfide	2,2'-dinitrodiphenyl disulfide unseparated mixture 2,4-nitrophenyl mercaptide (pure disulfide form)	85.2 } 93.7 8.5 } 90.0
3	4-nitrophenyl mercaptide	2,4'-dinitrodiphenyl disulfide	2,4'-dinitrodiphenyl disulfide impure 2,4'-disulfide 4-nitrophenyl mercaptide (iodine method)	70.8 15.2 100.0
4	2,4-dinitrodiphenyl mercaptide	2,4,2'-trinitrodiphenyl disulfide	2,4,2',4'-tetranitrodiphenyl disulfide 2,2'-dinitrodiphenyl disulfide mercaptides (iodine method) 2,4-dinitrophenyl mercaptide (disulfide form)	53.5 } 92.5 39.0 } 97.6 87.0
5	Phenyl mercaptide	2-nitrophenyl disulfide	diphenyl disulfide unseparated mixture of disulfides mixture of mercaptides (iodine method) o-nitrophenyl mercaptide (in form of disulfide)	46.0 } 99.0 53.0 } 96.0 78.0

(0.001 g-mol) in methyl alcohol (50 ml) and sodium disulfide (0.01 g-mol) in alcoholic solution (5 ml) at 45°. After 1.5 hours the solution of thiomercaptide is cooled to 20°, and a suspension of 0.001 g-mol of 2,4'-dinitrodiphenyl disulfide in 50 ml of methyl alcohol is added; the mixture is shaken for 2 hours. 2-Nitrophenyl thiomercaptide (expt. 2) and 2,4-dinitro thiomercaptide (expt. 3) are obtained, starting with o-dinitrobenzene and 1,2,4-chlorodinitrobenzene respectively at 0°. The reaction is complete after only 10 minutes; after this time, the suspension of disulfide is added, and the mixture shaken for 2 hours. The reaction mixtures are treated as usual.

The Reactions of 2,2'-Dinitrodiphenyl Trisulfide

Trisulfide and Sodium Sulfide. A suspension of 2,2'-dinitrodiphenyl trisulfide (0.204 g - 0.0006 g mol) in 100 ml of methyl alcohol is cooled to 0° and a solution of sodium sulfide (0.05 g - 0.0064 g-mol) in methyl alcohol (3 ml) is added; the mixture is allowed to stand for 1 hour with slight stirring. A red-

TABLE 4

Expt. No.	Original compounds		Found	
	Thiomercaptide	Disulfide	Name of compound	Yield (% theory)
1	4-nitrophenyl thiomercaptide	2,4-dinitrodiphenyl disulfide	2,4'-dinitrodiphenyl disulfide..	48.0
			2,2'-dinitrodiphenyl disulfide..	6.0
			unseparated mixture of disulfides	43.2
			4-nitrophenyl mercaptide (in form of disulfide	78.0
2	2-nitrophenyl thiomercaptide	2,4'-dinitrodiphenyl disulfide	2,2'-dinitrodiphenyl disulfide..	81.0
			unseparated mixture.....	19.5
			4-nitrophenyl mercaptide (iodine method).....	97.7
3	2,4-dinitrophenyl mercaptide	2,4,2'-trinitrodiphenyl disulfide	2,2'-dinitrodiphenyl disulfide..	63.7
			Tetranitrodiphenyl disulfide.....	32.0

violet color immediately appears, and the precipitate of trisulfide dissolves. To the solution an alcoholic solution of chlorodinitrobenzene (0.250 g - 0.0012 g-mol in 10 ml) is added, and the mixture is allowed to stand until the following day.

The precipitate (0.314 g) is filtered off, treated with carbon disulfide (almost no sulfur is present) and with acetone, which separates 2,4,2',4'-tetranitrodiphenyl disulfide (0.165 g) from 2,2'-dinitrodiphenyl disulfide (0.058 g). The alcoholic filtrate, which has an orange color, is evaporated under vacuum, giving a product (0.081 g) with an extended melting range (158-195°); this contains the disulfides mentioned.

Trisulfide and Thiophenolate. The conditions of the experiment were the same as previously, with the difference that thiophenolate (0.165 g - 0.0015 g-mol) was used instead of Na_2S , and the mixture was allowed to stand until the following day; it was then diluted with ice water and shaken with ether (in an atmosphere of nitrogen). Upon removal of the ether, diphenyl disulfide (0.090 g) was obtained. To the aqueous-alcoholic solution an alcoholic solution of chlorodinitrobenzene was added, to give 2,2',4'-trinitrodiphenyl sulfide (0.130 g).

Trisulfide and 2,4-Dinitrophenyl Mercaptide. To a suspension of the trisulfide (0.204 g - 0.006 g-mol) in alcohol (25 ml) an alcoholic solution of 2,4-dinitrophenyl mercaptide (0.135 g - 0.006 g-mol) in 25 ml was added, and the solution was allowed to stand for a day at room temperature. The precipitate was filtered off and washed with alcohol, then treated with carbon disulfide. Almost pure 2,2'-dinitrodiphenyl disulfide (0.168 g) was obtained, in a yield 93% of theory. Sulfur was present in the carbon disulfide solution.

Trisulfide and o-Nitrophenolate. To an alcoholic solution of o-nitrophenol

there was added a solution of caustic soda in alcohol, in an amount calculated to leave a small quantity of the free phenol. The solution obtained was added to a suspension of the trisulfide in methyl alcohol, using equimolecular amounts of reagents. On the following day, the precipitate was filtered off and treated with carbon disulfide to free it of sulfur. Pure 2,2'-dinitrodiphenyl disulfide was obtained in a yield 91% of theory.

SUMMARY

A study has been made of several reactions and complicated transformations of sulfide compounds of the benzene series.

It has been shown that the reduction cleavage of aromatic disulfides by alkaline sulfides, which is not correctly explained in the literature, takes place according to equations (XVI) and (XVII), to form, along with mercaptides, thiomercaptides (RS_2Na) and dithiomercaptides (RS_3Na).

Thiomercaptides have been obtained in the form of salts of the heavy metals, and some of their properties have been studied.

By the action of aryl thiomercaptides on halogen dinitro compounds with different radicals, there have been obtained (in the general case), contrary to expectations, not the mixed disulfides R_1S-SR_2 , but mixtures of the two simple disulfides. The course of the complicated transformations that take place in this case has been analyzed on the basis of concrete examples.

A study has been made of the reducing action of mercaptides and thiomercaptides on (mixed) disulfides.

Using 2,2'-dinitrodiphenyl trisulfide as an example, the instability of similar compounds has been shown; depending on the conditions, they can either undergo reduction cleavage or lose sulfur.

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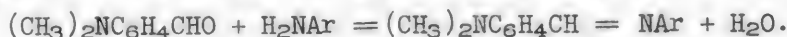
THE REACTION OF 4-DIMETHYLAMINO BENZALDEHYDE

WITH SECONDARY AROMATIC AMINES

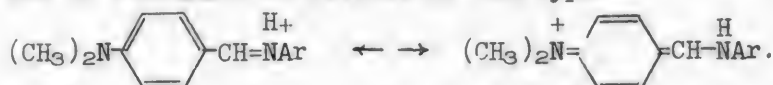
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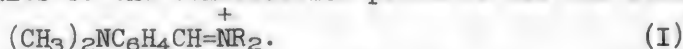
The literature contains many descriptions of Schiff bases, obtained from 4-dimethylaminobenzaldehyde and aromatic amines [1]:



Schiff bases are themselves of a weak yellow color; as a result of salt formation, the intensity of their color increases greatly. The color of the salts, apparently, is due to resonance of cations of the type:



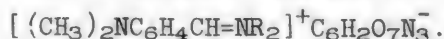
The color reaction of aromatic amines with 4-dimethylaminobenzaldehyde [2] and cinnamic aldehyde [3] depends on the formation of colored salts of Schiff bases. But 4-dimethylaminobenzaldehyde forms colored products not only with primary aromatic amines, but with secondary as well. We may assume that the colored cation of the salts of the condensation products has the structure:



The pseudobase (or carbinol base) $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CHOHNR}_2$ (II) will correspond to this cation. Salts and pseudobases formed by secondary amines with 4-dimethyl-amino benzaldehyde have up to the present, as far as we know, not been prepared.

In relation to the investigation of the qualitative reactions of amines, and in particular, to the study of the causes of the formation of color by 4-dimethylaminobenzaldehyde with secondary amines, we have carried out attempts to obtain individual salts of the colored reaction products of 4-dimethylaminobenzaldehyde with secondary aromatic amines. In the beginning, the experiments invariably led to negative results: upon the addition of mineral acids (HCl , HClO_4) to the alcoholic solution of 4-dimethylaminobenzaldehyde with secondary aromatic amines (diphenylamine, phenyl-2-naphthylamine) intensely colored solutions were obtained (usually deep yellow), from which it was impossible to isolate crystalline compounds. Either upon removal of the solvent by evaporation, or directly from the more concentrated solutions, darkly colored oils separated. It was impossible to doubt that a reaction took place between 4-dimethylaminobenzaldehyde and the amine, but it was equally impossible to isolate crystalline salts.

Only when toluene solutions of the components (aldehyde and amine) were used with picric acid did we succeed in isolating picrates of the new compounds. However, upon analysis, they showed a number of equivalents greater than that corresponding to the formula of the picrate of cation (I):



The number of equivalents found by titration with alkali corresponded to picrates

of the pseudobases (II), in other words to the picrates of 4-dimethylamino- α -hydroxybenzylamines:



The picrates isolated were colored orange or yellow-orange, and showed on test paper the reactions of 4-dimethylaminobenzaldehyde: with 1,4-diphenylenediamine in the vapor of formic acid, they gave a rose color. The attempts to isolate the free pseudobases in crystalline form appeared unsuccessful. Solutions which were supposed to contain the free bases showed the reactions of diphenylamine and 4-dimethylaminobenzaldehyde. Apparently, the free pseudobase was easily split into its components:



The literature gives indications of the existence of salts of Schiff base hydrates, formed by primary amines [4].

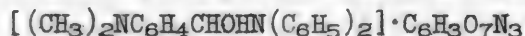
We have without doubt shown the existence of picrates of the substituted hydrates of Schiff bases. It remains, however, an open question whether the colored salts formed by mineral acids acting on 4-dimethylaminobenzaldehyde and secondary amines are identical with the salts of Schiff base hydrates, or whether we must ascribe to the salts a formula corresponding to formation from cation (1). The properties of the picrates we have obtained, most important of all their lightness of color, testify rather to the fact that the intensely colored salts are anhydride forms, and differ from the salts of Schiff base hydrates. The salts of the Schiff base hydrates can scarcely have an intense color, seeing that, for them, resonance of the cation is out of the question.

In our present communication, we describe for the first time the preparation of several picrates of N-substituted Schiff base hydrates, formed from 4-dimethylaminobenzaldehyde.

The investigation is being continued with the intention of obtaining as individual compounds the still unknown salts with the cation (I).

EXPERIMENTAL

The Picrate of N-(4-dimethylamino- α -hydroxybenzyl)-diphenylamine



1.7 g of diphenylamine (0.01 g-mol), 1.5 g of 4-dimethylaminobenzaldehyde (0.01 g-mol), and 2.5 g of picric acid (somewhat more than 0.01 g-mol) were dissolved with heating in 50 ml of toluene. The toluene solution, which had at first a deep color, grew lighter as the result of boiling for 5 minutes. The solution was filtered and cooled. Yellow-orange needles separated out. After standing overnight, the precipitate was filtered off, washed with 20 ml of toluene, and dried. The weight amounted to 2.87 g, or 58% of theory. Upon heating, the crystals darkened, and melted with decomposition at 154°. The substance was analyzed by titration with alkali in an alcohol solution with phenolphthalein indicator (10-12 drops of an alcoholic solution). The change of color was not very sharp, but after some practice, it could easily be detected.

0.8367 g substance: 15.05 ml 0.1 N NaOH.

1.1754 g substance: 21.18 ml 0.1 N NaOH.

Found: equiv. 556, 542.2.

$\text{C}_{21}\text{H}_{22}\text{ON}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$. Calculated: equiv. 547.51.

$\text{C}_{21}\text{H}_{21}\text{N}_2^+\text{C}_6\text{H}_2\text{O}_7\text{N}_3^-$. Calculated: equiv. 529.50.

No picrate was obtained from alcoholic solutions. Upon heating with

alkali, a colorless oil was obtained; a benzene solution of the oil, placed upon paper, gave a yellow color in the vapor of formic acid. With 1,4-phenylenediamine, the vapor of formic acid gave a rose color. With 4-nitrophenyldiazonium, it gave the reaction for diphenylamine. Under these conditions, diphenylamine picrate was not formed. In order that no doubt might remain about the nature of the product, the picrate of 4-dimethylaminobenzaldehyde was prepared.

Picrate of 4-Dimethylaminobenzaldehyde $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CHO} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$

1.5 g of 4-dimethylaminobenzaldehyde and 2.5 g of picric acid were dissolved with heating in 35 ml of toluene, and the solution was allowed to stand over night. Large lemon-yellow prisms with a violet luster separated out. After drying, they weighed 2.65 g. When alkali was poured over them, they turned orange. They melted with decomposition at 98°.

They were analyzed by titration with an alcoholic solution of alkali (phenolphthalein indicator).

0.8887 g substance: 23.78 ml 0.1 N NaOH.

Found: equiv. 373.8.

$\text{C}_9\text{H}_{11}\text{ON} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$. Calculated: equiv. 378.15.

The Dipicrate of N-(4-dimethylamino- α -hydroxybenzyl)-N-phenyl-2-naphthylamine



2.2 g of phenyl-2-naphthylamine (0.01 g-mol), 1.5 g of 4-dimethylaminobenzaldehyde (0.01 g-mol) and 2.5 g of picric acid (0.01 g-mol) were heated for 5 minutes in toluene solution. The solution was filtered and cooled; fine orange crystals separated out. The precipitate was filtered off and washed with 20 ml of toluene. After drying, it weighed 3.7 g. The picrate melted to give a dark liquid at 151°. It was analyzed by titration with alkali using phenolphthalein as an indicator (as before).

1.1539 g substance: 27.85 ml 0.1 N NaOH.

Found: equiv. 414.3.

$\text{C}_{25}\text{H}_{24}\text{ON}_2 \cdot 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$. Calculated: equiv. 413.15.

$\text{C}_{25}\text{H}_{24}\text{ON}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$. Calculated: equiv. 597.26.

The formula of the picrate with two molecules of picric acid was not unexpected. It was necessary to take account of the presence not only of the basic dimethylamino group, but also of the naphthyl radical. The picrate of N-phenyl-2-naphthylamine was fairly easily soluble, and did not precipitate from solution during the reaction of 2.5 g of picric acid and 2.8 g of N-phenyl-2-naphthylamine in 20 ml of toluene. Only after evaporation of the greater part of the toluene did the red-brown solution give dark brown crystals.

SUMMARY

1. It has been shown that a reaction takes place between 4-dimethylaminobenzaldehyde and secondary aromatic amines.

2. For the first time, picrates of substituted Schiff base hydrates have been isolated in crystalline form from 4-dimethylaminobenzaldehyde.

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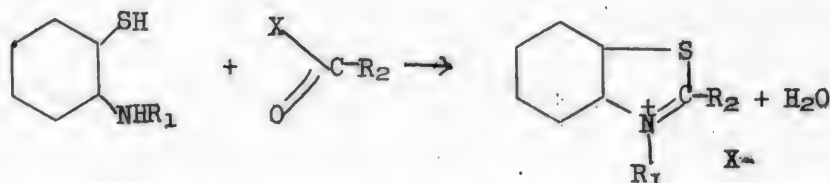
THE SYNTHESIS OF QUATERNARY SALTS OF BENZOTHAIAZOLE

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The quaternary salts of benzothiazole are formed in the usual way by the addition to benzothiazole of alkyl halides, esters of sulfuric acid, or of aryl sulfonic acids. The reaction requires heating of the mixture of components to high temperatures, and often takes place with tarring, and with small yields. It is generally impossible to use this method of preparation for quaternary salts of benzothiazole containing aryl groups on the hetero atom of nitrogen.

We have found that in a number of cases it is much more convenient to obtain quaternary salts of benzothiazole in another way, particularly, by the action of acid halides of carboxylic acid on N-alkyl or N-aryl aminothiophenols according to the equation:



The method is of a general character. It is equally suitable for the preparation of N-alkyl and N-aryl derivatives. The condensation takes place very easily, and with good yields. It is sufficient to mix equimolecular quantities of benzene solutions of the components in the cold for the reaction to begin at once, accompanied by the evolution of heat and clouding of the solution as a result of the water which separates out. The quaternary salt is precipitated in the form of an oil or a crystalline mass. It is washed with benzene or ether and then recrystallized from water or alcohol. As the majority of the alkyl chlorides of benzothiazole are hygroscopic, they are transformed into alkyl iodides by treatment of aqueous solutions of the salts with potassium iodide.

One of the conditions for the practical applicability of this method is the accessibility of the corresponding N-alkyl or N-aryl aminophenyl mercaptans. We have worked out an uncomplicated method for preparing them by the cleavage, with alcoholic alkali, of the quaternary salts of 2-alkylmercaptobenzothiazole. It is described in our following communication.

The condensation of o-aminothiophenol with carboxylic acids and their derivatives was described by Hofmann back in 1879 [1] and up to the present has remained one of the chief means of synthesis of bases of the benzothiazole series. However, if it is necessary to prepare not the base, but a quaternary salt, our method offers undoubted advantages over that of Hofmann. Instead of many hours of heating, as in Hofmann's method, of o-aminothiophenol with carboxylic acids in a sealed tube at a temperature above 100°, followed by purification of the base obtained and subsequent lengthy heating of this base with an alkyl halide,

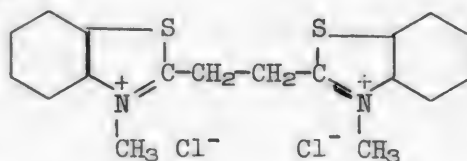
all necessary for the preparation of the quaternary salt, our method requires only a single simple operation: the mixing in the cold of two benzene solutions, one the acid chloride, and the other the corresponding N-alkyl-o-aminophenyl mercaptan.

The table lists the quaternary salts of benzothiazole and its derivatives which we have obtained from N-alkyl-o-aminophenyl mercaptans and the acid chlorides of monobasic acids.

The quaternary salts acquire peculiar properties as a result of the introduction of higher fatty acid chains. They have the character of inverted soaps. The methyl chlorides and ethyl iodides of these benzothiazole derivatives considerably lower the surface tension upon solution in water. Their aqueous solutions have a detergent action, and form a stable foam. If salts are added to the solutions, they are salted out like the usual soaps.

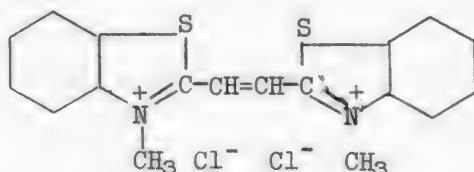
If formic or acetic acids are heated with o-methylaminothiophenol, no quaternary salts of benzothiazole are formed. However, if these acids are heated with methylaminothiophenol in the presence of concentrated hydrochloric acid, the methyl chlorides of benzothiazole and 2-methylbenzothiazole are obtained in yields of 60% and 45% respectively. In exactly the same way, if methylaminothiophenol is heated in a sealed tube with amides or esters of carboxylic acids in the presence of an excess of concentrated hydrochloric acid, quaternary salts are obtained in satisfactory yield. From acetamide and o-methylaminothiophenol, the methyl chloride of 2-methylbenzothiazole is obtained in 45% yield of theory; from ethyl acetate and methylaminothiophenol, in 65% yield. The reactions of o-alkylaminophenyl mercaptans with the anhydrides of carboxylic acids are complicated by the simultaneous formation of carbocyanines.

The condensation of N-methylaminothiophenol was also carried out with the acid chlorides of dibasic acids, particularly with succinyl chloride and fumaryl chloride. In the first case, the bis-(methyl chloride)- of bis[benzothiazolyl-(2)]-1,2-ethane was obtained.



m.p. 285-286°

The second acid chloride gave the previously unknown bis-(methyl chloride) of bis-[benzothiazolyl-(2)]-1,2-ethylene.



decomposes above 350°

These biquaternary salts upon treatment with alkali gave precipitates which did not contain halogen. In the first case, an unsaturated bismethylene base was obtained, with a yellow color. The structure of the second base was not determined. A molecular weight determination by Rast's method showed that the action of the alkali upon the biquaternary salt of bis-benzothiazolyethylene had formed a polymer.

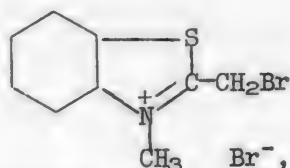
A detailed investigation of the condensation of N-alkyl and N-aryl amino-thiophenols with bis(-acid chlorides) of various dibasic carboxylic acids has been

been carried out by I.K.Ushenko [6]. A.I.Kiprianov and I.K.Ushenko synthesized and described [7] a number of phenyl halides of 2-alkylbenzothiazole, using the condensation of N-phenyl-o-aminophenyl mercaptans with the acid chlorides according to our method.

Expt. No.	Components of the reaction		Condensation products			M.p. according to literature data
	acid chlorides	alkyl in $\text{C}_6\text{H}_4\begin{smallmatrix} \text{SH} \\ \text{NHA} \end{smallmatrix}$	Quaternary salt	Yield (% of theor.)	m.p.	
1	acetyl chloride	methyl	Methyl iodide of 2-methylbenzothiazole	83	222°	222° [2]
2	same	ethyl	Ethyl iodide of 2-methylbenzothiazole	72	191°	190° [3]
3	same	carboxy-methyl	Carboxymethyl iodide of 2-methylbenzothiazole	45	267	
4	same	benzyl	Benzyl iodide of 2-methylbenzothiazole	66	201	
5	propionyl chloride	methyl	Methyl iodide of 2-methylbenzothiazole	78	175.5	175 [4]
6	same	ethyl	Ethyl iodide of 2-ethylbenzothiazole	70	193	192-193[5]
7	butyryl chloride	methyl	Methyl iodide of 2-propylbenzothiazole	75	215	
8	same	ethyl	Ethyl iodide of 2-propylbenzothiazole	62	181	[4]
9	caproyl chloride	methyl	Methyl iodide of 2-amylobenzothiazole..	73	189	
10	caprylyl chloride	methyl	Methyl iodide of 2-heptylbenzothiazole	62	168	
11	capryl chloride	methyl	Methyl iodide of 2-nonylbenzothiazole.	55	232	
12	lauryl chloride	methyl	Methyl iodide of 2-undecylbenzothiazole	69	217	
13	same	benzyl	Benzyl iodide of 2-undecylbenzothiazole	71	205	
14	palmityl chloride	methyl	Methyl iodide of 2-pentadecylbenzothiazole	60	320 with decomp	
15	same	ethyl	Ethyl iodide of 2-pentadecylbenzothiazole.....	51	316 with decomp	
16	same	benzyl	Benzyl iodide of 2-pentadecylbenzothiazole.....	59	288	
17	stearyl chloride	methyl	Methyl iodide of 2-heptadecylbenzothiazole.....	58	323 with decomp	

Expt. No.	Components of the reaction		Condensation products			M.p. according to literature data
	acid chlorides	alkyl in $\text{C}_6\text{H}_4\begin{smallmatrix} \text{SH} \\ \text{NHAlk} \end{smallmatrix}$	Quaternary salt	Yield (% of theory)	m.p.	
18	stearyl chloride	benzyl	Benzyl iodide of 2-heptadecyl-benzothiazole...	45	293	
19	benzoyl chloride	methyl	Methyl iodide of 2-phenyl-benzothiazole...	84	198	
20	phenylacetyl chloride	methyl	Methyl iodide of 2-benzylbenzothiazole.....	59	195-196	

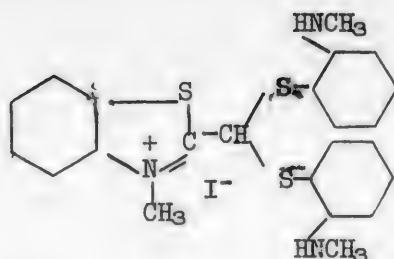
As is known, α -halogen acids condense with o-aminothiophenol to give not thiazole, but thiazine derivatives. In distinction from aminothiophenol, the latter's N-methyl derivative gives, with the acid bromide of bromoacetic acid, the methyl bromide of 2-bromomethylbenzothiazole:



whose formation is confirmed by the properties of the salt obtained and by its analysis. In fact, we were obliged to change our method of experiment somewhat, using more than a double excess of bromoacetyl bromide and gradually adding o-methylaminothiophenol to it, in order that the acid bromide might always be in great excess. The comparatively low yield of the quaternary salt (36% of theory), and the formation of a large amount of uncrystallizable oil showed that the reaction also proceeded in other direction.

In the condensation of the esters of α -halogen carboxylic acids with N-methyl-o-aminothiophenol, we obtained only benzothiazole derivatives. Thus, for example, the action of methylaminophenyl mercaptan on the ethyl esters of α -bromoacetic, α -bromopropionic, and α -bromobutyric acids gave N-alkylbenzothiazinone-3. The preparation and properties of these new heterocyclic ketones will be described in a separate communication.

It was of interest to investigate the process of condensation of dichloroacetyl chloride with methylaminothiophenol. Even when a triple excess of the acid chloride was used, we were unable to isolate the quaternary salt of 2-dichloromethylbenzothiazole. The product obtained gave the characteristic reactions for a secondary amino group (it could be acetylated, and it formed a nitroso-compound with nitrous acid). From the analytical data, it contained 7.37% of nitrogen and 22.30% of iodine. On the basis of these figures, we ascribed to the compound the structure of a methyl iodide of 2-bis-(o-methylaminophenylmercapto)-methylaminobenzothiazole:



Calculated %: N 7.44. I 22.52

Quaternary salts of benzoxazole were obtained in a manner similar to the quaternary salts of benzothiazole. N-Ethyl-o-aminophenol [8], upon condensation with acetyl chloride, gave the ethyl iodide of 2-methyl-benzoxazole, with m.p. 197°.

EXPERIMENTAL

The Methyl Iodide of 2-Methylbenzothiazole. a) To a solution of 1.39 g of methylaminothiophenol in 5 ml of benzene, there was added a solution of 0.8 g (1 mole) of acetyl chloride in 2 ml of benzene. The mixture spontaneously evolved heat and precipitated a heavy, pale-yellow oil, which crystallized upon cooling to give a colorless crystalline mass. The crystals were filtered off and washed with benzene. The hygroscopic methyl chloride salt was dissolved in water, and to the solution was added a concentrated solution of potassium iodide. The methyl iodide salt precipitated. It was recrystallized from water. It formed colorless crystals with m.p. 221-222°. A mixed test with the methyl iodide of 2-methylbenzothiazole, obtained by heating the base with methyl iodide, gave no m.p. depression. Yield 83% of theory.

b) 1.39 g of methylaminothiophenol, 0.6 g of glacial acetic acid, and 1 ml of concentrated hydrochloric acid were boiled with a reflux condenser for 2 hours. The hardened crystalline mass was carefully washed with benzene, dissolved in water, and treated with potassium iodide. Colorless leaves were obtained, with m.p. 221°. After recrystallization from alcohol, the yield was 45% of theory.

c) 1.39 g of methylaminothiophenol, 0.65 g (1.1 mole) of acetamide, and 2.6 ml of concentrated hydrochloric acid were heated in a sealed tube at 120° for 2 hours. Yield of methyl iodide salt, with m.p. 221-222°, 45% of theory.

d) 1.39 g of methylaminothiophenol, 0.97 g (1.1 mole) of ethyl acetate, and 2.6 ml of concentrated hydrochloric acid were heated under the same conditions. Yield of methyl iodide salt 1.89 g., or 65% of theory.

The Carboxymethyl Iodide of 2-Methylbenzothiazole. 1.83 g of N-carboxymethylaminothiophenol (cf. our following communication) in 5 ml of ether was mixed with a solution of 0.7 g of acetyl chloride in 3 ml of ether. The yellow crystalline substance which precipitated out was filtered off, washed with ether, and converted into the iodide by the action of potassium iodide. Yield of the salt after recrystallization from alcohol 1.5 g, or 45% of theory. M.p. 267° (with decomp.)

Found %: N 4.07.

$C_{10}H_{10}O_2NSI$. Calculated %: N 4.18.

The Ethyl Iodide of 2-Methylbenzothiazole was obtained in the same way as the methyl iodide of 2-methylbenzothiazole from equivalent amounts of o-ethylaminothiophenol and acetyl chloride in benzene. It was in the form of shining white leaves with m.p. 191°, and gave no m.p. depression on mixing with the ethyl iodide of 2-methylbenzothiazole obtained in the usual way. Yield 72% of theory.

The Benzyl Iodide of 2-Methylbenzothiazole. This was obtained from 1.08 g

of N-benzyl-o-aminothiophenol and 0.34 g of acetyl chloride, in the same way as before. Yield 1.2 g, or 66% of theory. M.p. 201°.

Found %: N 3.93; I 34.74.
 $C_{15}H_{14}NSI$. Calculated %: N 3.81; I 34.63.

The Methyl Iodide of 2-Ethylbenzothiazole. This was obtained from 1.4 g of methylamino thiophenol and 1.1 g of propionyl chloride in benzene. After recrystallization from water, colorless leaves were obtained with m.p. 175.5°. Yield 2.5 g, or 78% of theory.

The same product was obtained by heating in a sealed tube 1.39 g of methylamino thiophenol, 1.12 g (1.1 mole) of ethyl propionate, and 2.6 ml of concentrated hydrochloric acid for 4 hours at 120-140°. Yield of methyl iodide salt 2.7 g, or 68% of theory.

The Ethyl Iodide of 2-Ethylbenzothiazole. This was obtained from 1.5 g of N-ethylamino thiophenol and 1.1 g of propionyl chloride. Yield 70% of theory; m.p. 193°.

Found %: N 4.32.
 $C_{11}H_{14}NSI$. Calculated %: N 4.39.

The Methyl Iodide of 2-Propylbenzothiazole. This was obtained from 1.4 g of butyryl chloride and 1.4 g of methylaminothiophenol. Yield 75% of theory. The product was in the form of colorless leaves. M.p. 215°.

The same product was obtained from methylaminothiophenol and ethyl butyrate by heating in a sealed tube at 120-140° for 5 hours. Yield 50% of theory.

The Ethyl Iodide of 2-Propylbenzothiazole. This was obtained from ethylaminothiophenol and butyryl chloride in benzene, in the form of colorless leaves with m.p. 181-182°. Yield 62% of theory.

Found %: N 4.30.
 $C_{12}H_{16}NSI$. Calculated %: N 4.20.

The Methyl Iodide of 2-Heptylbenzothiazole. This was obtained from methylaminothiophenol and caprylyl chloride. The methyl iodide salt is easily soluble in alcohol, acetone, and water, making it difficult to recrystallize from these solvents. The alcoholic solution of the compound was boiled with animal charcoal, filtered, and precipitated with ether. Yield of salt 54% of theory. M.p. 168°.

Found %: N 3.77; I 34.33.
 $C_{15}H_{22}NSI$. Calculated %: N 3.89; I 34.00.

The Methyl Iodide of 2-Amylbenzothiazole. This was obtained from methylaminothiophenol and caproyl chloride. After recrystallization from alcohol, colorless leaves were obtained, with m.p. 189°. Yield 73% of theory.

Found %: I 36.50.
 $C_{13}H_{18}NSI$. Calculated %: I 36.60

The Methyl Iodide of 2-Nonylbenzothiazole. This was obtained from methylaminothiophenol and capryl chloride in a yield of 50% of theory. M.p. 232°.

Found %: N 3.39; I 31.65.
 $C_{17}H_{28}NSI$. Calculated %: N 3.49; I 31.51.

The Methyl Iodide of 2-Undecylbenzothiazole. This was obtained from methylamino thiophenol and lauryl chloride in a yield of 44% of theory. M.p. 217°.

Found %: N 3.32; I 29.63.
 $C_{19}H_{30}NSI$. Calculated %: N 3.25; I 29.49.

The Benzyl Iodide of 2-Undecylbenzothiazole. This was obtained from benzyl-

aminothiophenol and lauryl chloride. The benzyl chloride salt melted at 192°, the benzyl iodide salt at 205°. Yield 71% of theory.

Found %: N 2.68; I 25.22.

$C_{25}H_{34}NSI$. Calculated %: N 2.76; I 25.05.

The Methyl Iodide of 2-Pentadecylbenzothiazole. This was obtained from palmityl chloride and methylaminothiophenol in benzene. Yield of chloride 68% of theory, m.p. of chloride 289°. The methyl iodide salt was in the form of colorless, shining leaves with m.p. 320° (with decomp). Yield 60% of theory.

Found %: N 2.79; I 25.97.

$C_{23}H_{38}NSI$. Calculated %: N 2.87; I 26.07.

The Ethyl Iodide of 2-Pentadecylbenzothiazole. This was obtained from ethylaminothiomercaptan and palmityl chloride. The ethyl chloride salt was in the form of colorless yellowish leaves, similar to palmitic acid. After recrystallization from alcohol, the m.p. was 295-297° (with decomp.). The ethyl iodide salt was in the form of white shining leaves with temperature of decomposition about 330°. Yield 50% of theory.

Found %: N 2.77.

$C_{24}H_{40}NSI$. Calculated %: N 2.80.

The Benzyl Iodide of 2-Pentadecylbenzothiazole. This was obtained from benzylaminothiophenol and palmityl chloride in ether. The benzyl chloride salt, recrystallized from alcohol, had m.p. 254° (with decomp.). The benzyl iodide salt was in the form of colorless leaves with m.p. 288° (with decomp). Yield 59% of theory.

Found %: I 22.28

$C_{28}H_{42}NSI$. Calculated %: I 22.55.

The Methyl Iodide of 2-Heptadecylbenzothiazole. The methyl chloride salt was obtained from methylaminophenylmercaptan and stearyl chloride in ether in the form of snow-white platelets with m.p. 295°. The methyl iodide salt was in the form of yellowish plates with decomposition temperature 323°. Yield of methyl iodide salt, 58% of theory.

Found %: N 2.82; I 25.40.

$C_{25}H_{42}NSI$. Calculated %: N 2.71; I 25.63.

The Benzyl Iodide of 2-Heptadecylbenzothiazole. This was obtained from benzylaminothiophenol and stearyl chloride in ether. The chloride was in the form of fine colorless platelets, with decomposition temperature 298°. The iodide was in the form of platelets with m.p. 307° (with decomp). Yield 45% of theory.

Found %: I 21.35.

$C_{31}H_{46}NSI$. Calculated %: I 21.48.

The Methyl Iodide of 2-Phenylbenzothiazole. This was obtained from methylaminothiophenol and benzoyl chloride in benzene. It was in the form of yellow shining leaves with m.p. 198°. Yield 84% of theory.

Found %: N 5.66.

$C_{14}H_{12}NSI$. Calculated %: N 5.53.

The Methyl Iodide of 2-Benzylbenzothiazole. This was obtained from methylaminophenyl mercaptan and phenylacetyl chloride in benzene. It was in the form of light yellow needles with m.p. 196°. Yield 58% of theory.

The Bis(Methyl Chloride) of Bis-(Benzothiazolyl)-Ethane. This was obtained from methylaminothiophenol and succinyl chloride in toluene upon cooling. After recrystallization, the yield was 53% of theory. The product was in the form of

pale cream-colored platelets with m.p. 285-286°. It was slightly soluble in water, very soluble in hot alcohol. The bis-(methyl iodide) had m.p. 310° (with decomp).

Found %: N 7.07.

$C_{18}H_{18}N_2S_2Cl_2$. Calculated %: N 7.05.

From the aqueous solution of the methyl chloride salt, alkali precipitated the bis-methylene base with a clear yellow color.

The Bis-(Methyl Chloride) of Bis-(benzothiazolyl)-1,2-ethylene. The bis-(methyl chloride) was obtained from 2.8 g of methylaminothiophenol and 1.5 g (0.5 mole) of fumaryl chloride in benzene with intense cooling. The bis-(methyl chloride) was in the form of fine yellow needles with decomposition temperature above 300°. The bis-(methyl iodide) was in the form of brownish-red needles, which decomposed upon heating, but did not melt.

Found %: N 6.94.

$C_{18}H_{18}N_2S_2Cl_2$. Calculated %: N 7.08.

Upon the addition of a solution of alkali to the aqueous solution of the bis-(methyl chloride), a light yellow amorphous substance could be precipitated. Upon heating, this decomposed, but did not melt. The compound, reprecipitated by ligroin from dichloroethane, contained no chlorine. It dissolved in alcohol and chloroform, as well as in concentrated hydrochloric acid.

Found %: N 8.55.

$C_{18}H_{14}N_2S_2$. Calculated %: N 8.69.

A determination of the molecular weight by Rast's method showed that it had approximately tripled its previous molecular weight.

Found: M 998.

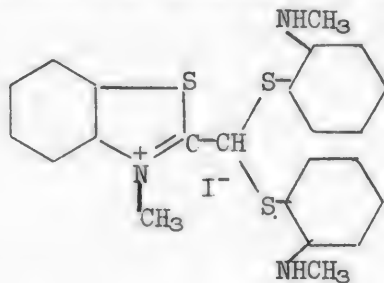
$C_{18}H_{14}N_2S_2$. Calculated: M 322.

The Methyl Bromide of 2-Bromomethylbenzothiazole. 1.39 g of methylaminothiophenol in 3 ml of benzene was gradually added to 4.04 g (2 moles) of bromoacetyl bromide in 5 ml of benzene. After a half hour of heating on an air bath, the oil which had precipitated almost completely crystallized. The light yellow crystals were filtered off, washed with benzene, and dried. After recrystallization from water, a white crystalline salt was obtained with m.p. 197° (with decomp.). Yield 1.2 g, or 36% of theory. The quaternary salt was hydrolyzed by water, therefore the recrystallization from water was carried out after the solution had been acidified with hydrobromic acid.

Found %: N 4.47.

$C_9H_9NSBr_2$. Calculated %: N 4.33.

The Methyl Iodide of 2-Bis-(o-methylaminophenylmercapto)-methylbenzothiazole:



1 g of methylaminothiophenol in 5 ml of benzene was gradually added to a solution of 3 g (3 moles) of dichloroacetyl chloride in 5 ml of benzene. The crystals

which precipitated out were washed with benzene, and dissolved in water. The quaternary salt was precipitated by the addition of potassium iodide. After recrystallization from alcohol with animal charcoal, 0.5 g of the methyl iodide salt was obtained (30% of theory), with m.p. 282-285° (with decomp.)

Found %: N 7.34; I 22.30.

$C_{23}I_2M_3S_3I$. Calculated %: N 7.44; I 22.52.

The Methyl Iodide of Benzothiazole. 1.39 g of methylaminothiophenol, 0.6 g (1 mole) of 92% formic acid, and 1 ml of concentrated hydrochloric acid were boiled for a half hour. The crystalline precipitate was dissolved in water and treated with potassium iodide. The methyl iodide salt obtained melted at 211°. A mixed test with the methyl iodide salt obtained in the usual way gave no m.p. depression. After recrystallization from alcohol, the yield was 60% of theory.

SUMMARY

We have suggested a method for the preparation of quaternary salts of benzothiazole derivatives. This method, which is convenient for purposes of synthesis, consists of the condensation of acid chlorides of carboxylic acids with N-alkyl and N-aryl amino-o-phenyl mercaptans. The reaction takes place in the cold and gives good yields. By means of it, it is possible to obtain with ease quaternary salts of benzothiazole containing aryl groups upon the nitrogen hetero atom. We have obtained and described 23 quaternary salts of benzothiazole, among them the biquaternary salts obtained from acid chlorides of dicarboxylic acids.

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N-ALKYL AND N-ARYL o-AMINOPHENYL MERCAPTANS

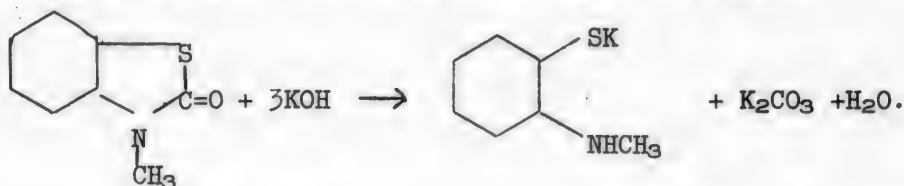
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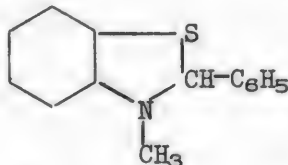
N-Alkyl and N-aryl o-aminophenyl mercaptans are almost unknown. The sole representative of this class of compounds, N-methyl-o-aminophenyl mercaptan, was prepared by Harries and Lowenstein [1] and then by Mills, Clark, and Aeschlimann [2] by the alkaline fusion of benzothiazoloneimine, but was not isolated in pure form; only derivatives of this compound were analyzed.

We were able to show that the cleavage of quaternary salts of benzothiazole with alcoholic alkali was a convenient method for the preparation of individual N-alkyl and N-aryl aminothiophenols. It is known that benzothiazole itself can be cleaved to form o-aminothiophenol by alkaline fusion [3]; however the quaternary salts of benzothiazole are cleaved much more easily. They are converted by the action of alkali into benzothiazoline derivatives, and the thiazoline ring, due to its less strongly expressed aromatic character, is considerably less stable than the thiazole ring.

As our experiments have shown, ten minutes of boiling of N-methylbenzothiazolone with an alcoholic solution of caustic potash is sufficient to give a quantitative yield of N-methylaminothiophenol, according to the equation:



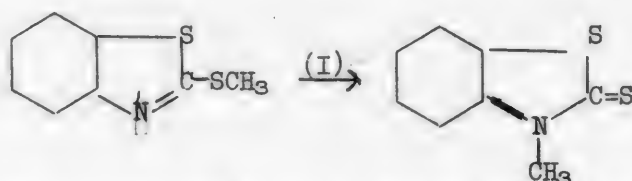
Somewhat more difficult, but still giving excellent yields of methylaminophenyl mercaptan, are the reactions of alcoholic alkali with 3-methylbenzothiazoloneimine and 3-methylbenzothiazolonethione. 3-Methylbenzothiazolines [4] that we have synthesized, for example,



are cleaved by alkali just as easily. One of us and I.K.Ushenko [5] cleaved N-phenylbenzothiazolone and its imine and for the first time obtained N-phenyl-o-aminothiophenol with yields of 77% and 67%, respectively. Thus, N-alkyl and N-aryl benzothiazolones, their imines, and their thiones, can serve as convenient starting materials for the preparation of o-aminophenyl mercaptans monoalkylated or monoarylated at the amino group.

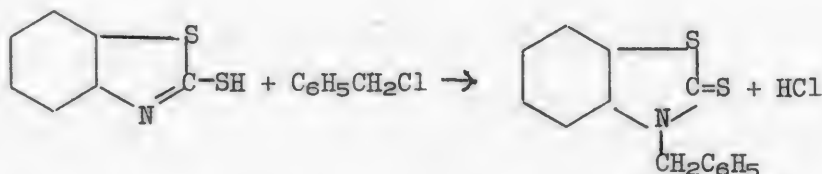
In practice, the simplest compound of all to use for this purpose is "Captax" (technical 2-mercaptobenzothiazole). We alkylated it upon the sulfur atom, for example, by the action of dimethyl sulfate in alkaline solution, then converted it into the quaternary salt by heating with alkyl halides or dialkyl sulfates. By the action of concentrated alkali in the cold, according to the method of Sexton [8], the quaternary salts were transformed into N-alkylbenzothiazolones, which are oils insoluble in alkali. The thiazolones were boiled with alcoholic alkali. We used concentrated solutions, but the cleavage takes place smoothly even with a 5% solution of caustic potash in alcohol. The reaction was completed in 30 to 60 minutes, and the potash was then filtered off, the alcohol driven off by evaporation, and the residue in the flask dissolved in water and neutralized with hydrochloric acid. The precipitated alkylaminothiophenol was purified by distillation in vacuum. We thus obtained N-methyl, N-ethyl, and N-carboxymethyl o-aminophenyl mercaptans.

A convenient variant of this method is the following. The 2-alkylmercaptobenzothiazole is isomerized by heating with a small quantity of iodine [7] to give the N-alkylbenzothiazolonethione:



the unchanged 2-alkylmercaptobenzothiazole is washed out of the thione with concentrated hydrochloric acid and is regenerated, while the thione is subjected to cleavage with alcoholic alkali.

We obtained N-benzylbenzothiazolonethione by heating 2-mercaptobenzothiazole with benzyl chloride [7]:



As this compound is only slightly soluble in alcoholic alkali, it was cleaved by an alkaline fusion, giving N-benzylaminothiophenol in a yield 43% of theory.

If alkaline fusion is used to obtain methylaminothiophenol from the methyl methosulfate of 2-methylmercaptobenzothiazole, the reaction takes place with a much worse yield (25% of theory) than in the case of cleavage with alcoholic alkali. The mineral salts which are formed make the fusion more difficult to carry out, and the free access of air leads to the formation of disulfides.

To obtain N-phenyl-o-aminothiophenol [5], we treated N-diphenylthiourea to produce ring-formation, giving the phenyl bromide of 2-aminobenzothiazole. The latter compound was treated with ammonia, and the imine formed was either subjected to the action of alcoholic alkali directly, or first converted into the thiazolone [8] by means of nitrosoimine.

N-Methyl, n-ethyl, and N-benzyl o-aminophenyl mercaptans are pale yellow oils with a specific gravity greater than one. N-Carboxymethylaminothiophenol and N-phenylaminothiophenol are yellowish crystalline compounds with m.p. 132° and 41° respectively. All have unpleasant mercaptan odors, and like the amino-

thiophenols, cause eczema upon contact with the skin. These compounds are soluble in the majority of organic solvents, and N-carboxymethylaminophenyl mercaptan, in addition, is soluble in hot water.

N-Methyl, N-ethyl, N-benzyl, and N-phenyl aminophenyl mercaptans are soluble both in acids and in alkalies. Except for the N-carboxymethyl derivative, they are extremely easy to oxidize, especially in alkaline medium; this must be taken into account in their preparation and storage. They can be kept for a long time if the access of air is prevented.

These compounds form picrates, iodides, and perchlorates which are difficultly soluble in water. In alcoholic solutions, the N-alkylaminothiophenols give, with salts of lead, tin, silver, antimony, and copper, colored precipitates which are insoluble in water.

All the N-alkyl and N-aryl aminothiophenols are extremely reactive substances, whose use has permitted us to obtain a number of benzothiazole [9], benzothiazoline [4], and benzothiazine, derivatives which are difficult to obtain in any other way.

EXPERIMENTAL

N-Methyl-o-aminophenyl Mercaptan

The first member of the homologous series of N-alkylaminophenyl mercaptans can be obtained by the alkaline cleavage of N-methylbenzothiazolone, N-methylbenzothiazolethione, N-methylbenzothiazoloneimine, and N-methylbenzothiazoloneanil.

N-Methylbenzothiazolone-2 was obtained from Captax. 100 g of Captax was dissolved in 360 ml of 10% caustic soda solution. The insoluble precipitate was filtered off, and to the transparent solution there was added gradually, with vigorous stirring, 76 g of dimethyl sulfate. The oil which settled out on the bottom of the flask crystallized. It was distilled in vacuum. There was obtained 76 g (70% of theory) of the colorless 2-methylmercaptobenzothiazole, with m.p. 52° and b.p. 174-176° at 20 mm.

The methyl methosulfate of 2-methylmercaptobenzothiazole was obtained by heating equivalent quantities of methylmercaptobenzothiazole and freshly distilled dimethyl sulfate on the water bath for 2 hours. The crystalline light cream-colored mass deliquesced in the air.

100 g of the quaternary salt in 200 ml of water was treated with 62 ml of a 40% caustic soda solution (2.2 moles). The oil which precipitated out was separated from the water layer. It was a mixture of pseudo base, thione, and thiazolone. The mixture was subjected to cleavage with alcoholic alkali without separation. In order to isolate the pure thiazolone, the partially crystallized product was washed with ligroin to remove the oily portion. The thiazolone was thus obtained in almost pure form with m.p. 75-76° in 32 g yield, or 61% of theory. If the solvent was distilled off from the ligroin extract, and the oil that remained was treated with hydrochloric acid, there was left a small amount of product insoluble in hydrochloric acid; after recrystallization from alcohol, this melted at 89-90°. A mixed test with 3-methylbenzothiazolethione showed no m.p. depression. The part of the product which had gone into the hydrochloric acid solution was concentrated by evaporation, and potassium iodide was added to the solution. The salt which precipitated had m.p. 139° and was identical with the methyl iodide of 2-methylmercaptobenzothiazole.

N-Methylbenzothiazolethione-2 was prepared from 20 g of 2-methylmercaptobenzothiazole and 0.2 g of crystalline iodine by heating in a sealed tube at 210-220° for 4 hours. After recrystallization from alcohol, the m.p. was 88-90°. Yield 16 g, or 80% of theory.

N-Methylbenzothiazoloneimine-2 was obtained by ring-formation in as-methyl-phenylthiourea, by Besthorn's method [10]. Yield of compound with m.p. 123° was 69% of theory.

N-Methylbenzothiazoloneanil-2 was synthesized from phenylcarbylamine dichloride [11] by condensation with N-methylaminothiophenol. 5 g of N-methyl-o-aminothiophenol in 15 ml of benzene and 6.3 g of the dichloride of phenylcarbylamine in 8 ml of benzene were mixed with vigorous cooling. A vigorous reaction took place accompanied by boiling of the benzene. A dark lower layer separated. It was washed with benzene, dissolved in water, and neutralized with ammonia. After recrystallization from alcohol treated with activated charcoal, 3.1 g of a colorless crystalline product with m.p. 154° was obtained.

Found %: N 11.42.

$C_{14}H_{12}N_2S$. Calculated %: N 11.66.

N-Methyl-o-aminophenyl Mercaptan from N-Methylbenzothiazolone

32.5 g of N-methylbenzothiazolone was dissolved in 100 ml of hot alcohol; this solution was mixed with 100 ml of an alcoholic solution of caustic potash (33 g of caustic potash, 3 moles), and the mixture was boiled on the water bath for 10 to 20 minutes. The precipitated potash was filtered off with suction on a Buchner funnel and washed with 100 ml of alcohol. The alcohol was driven off from the filtrate and the residue dissolved in 100 ml of water and neutralized with concentrated hydrochloric acid while the solution was cooled. The light yellow oil which separated out was extracted with benzene and the solvent driven off. 24 g of a light yellow oil was obtained; after distillation in vacuum at 126° and 18 mm, 23 g remained, or 84% of theory, calculated on the basis of the benzothiazolone (59% of theory on the basis of the quaternary salt). For cleavage of the unpurified benzothiazolone, which contained the thione and the pseudo base, 6 moles of alcoholic caustic potash were used. The duration of boiling was increased to 30 minutes (hood!). The yield of pure mercaptan was 31.5 g, or 70%, calculated on the basis of the quaternary salt.

N-Methyl-o-aminothiophenol from N-Methylbenzothiazolethione

16 g of N-methylbenzothiazolethione was dissolved with heating in 100 ml of alcohol and mixed with 100 ml of a solution of caustic potash in alcohol (29 g of caustic potash, or 6 moles). The mixture was boiled for 2 hours. Yield 9.3 g, or 76% of theory.

N-Methyl-o-aminothiophenol from N-methylbenzothiazoloneimine

19 g of methylbenzothiazoloneimine in 60 ml of alcohol and 39 g of caustic potash in 120 ml of alcohol were boiled for 2 hours until no more ammonia was given off. Yield 11.7 g, or 63.4% of theory. The cleavage of N-methylbenzothiazoloneanil requires 6 moles of caustic potash in alcohol. The product was oxidized with hydrogen peroxide and isolated in the form of the bis-(o-methylaminophenyl) disulfide in a yield 83% of theory. M.p. of the disulfide, 68°.

N-methyl-o-aminothiophenol was a light yellow oil, b.p. 142-143° at 30 mm., and 126-127° at 18 mm. In the air, it was quickly oxidized to the disulfide.

Found %: N 9.94, 9.97.

C_7H_9NS . Calculated %: N 10.07.

The picrate was in the form of yellow plates with m.p. 140°, the iodide, pale yellow needles with m.p. 110°. The chloride was in the form of hygroscopic small white leaves. N,S-Dimethylaminophenyl mercaptan was a colorless liquid with b.p. 127° at 11 mm. N,S-Dimethylacetylaminothiophenol was in the form of crystals with m.p. 81-82° [9].

N-Ethyl-o-aminophenyl Mercaptan

N-Ethylbenzothiazolone-2 was obtained from Captax. 20 g of Captax was dissolved in 50 ml of 10% caustic soda, and to the solution, with cooling and stirring, there was added 20 g of diethyl sulfate. The oil which precipitated out was distilled in vacuum. Yield of crystalline 2-ethylmercaptobenzothiazole, 16.2 g, or 66% of theory. This compound was heated with an equimolecular quantity of diethyl sulfate for 5 hours at 110-120°. The yield of quaternary salt was quantitative. To a solution of 15.3 g of the salt obtained in 50 ml of water there was added a solution of 4 g of caustic soda in 16 ml of water. The oil which separated out was removed and treated with alcoholic alkali in order to obtain N-ethylaminothiophenol. By means of washing with ligroin, it was possible to obtain from the oil a crystalline substance with m.p. 58°, corresponding in properties to N-ethylbenzothiazolone.

N-Ethylbenzothiazolethione-2 was obtained from 16 g of 2-ethylmercaptobenzothiazole and 0.5 g of crystalline iodine by heating in a sealed tube for 3 hours at 210°. The isomerization product was ground in a mortar and washed with concentrated hydrochloric acid, then recrystallized from alcohol. Yield 10.4 g, or 51% of theory; m.p. 73-75°.

N-Ethyl-o-aminothiophenol was obtained from N-ethylbenzothiazolone by boiling with 6 moles of alcoholic caustic potash for 30 minutes. At 20 mm, within the limits from 129-130°, there distilled over an almost colorless oil. Yield 73% of theory calculated on the basis of quaternary salt. On storage, the oil slowly turned yellow; in the air, it was quickly oxidized to the disulfide with m.p. 72°.

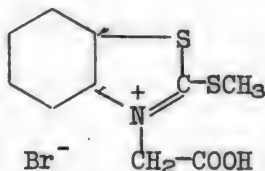
Found %: N 9.01.

$C_8H_{11}NS$. Calculated %: N 9.15.

The same product was obtained in 77% yield from N-ethylbenzothiazolethione by boiling for 2 hours with 6 moles of alcoholic caustic potash.

N-Carboxymethyl-o-aminophenyl Mercaptan

This mercaptan was obtained by us by the cleavage with alkaline alkali of the quaternary salt of the carboxymethyl bromide of 2-methylmercaptobenzothiazole:



The latter was obtained by heating equimolar quantities of 2-methylmercaptobenzothiazole and bromoacetic acid on a water bath in a sealed tube for 8 hours. The quaternary salt was a solid, vitreous mass, extremely soluble in water, and deliquescent when left in the air. The carboxymethyl iodide melted at 183°, with decomposition. The perchlorate was in the form of colorless needles. 23 g of the carboxymethyl bromide was dissolved in 60 ml of alcohol and mixed with a solution of 34 g of caustic potash (9 moles) in 105 ml of alcohol. A white crystalline precipitate immediately formed. After boiling for 2 hours, the precipitate was filtered off, washed with alcohol, and the alcohol driven off from the filtrate. The solid residue in the flask was dissolved in 40 ml of water and neutralized with concentrated hydrochloric acid until the reaction was neutral to phenolphthalein. During this process, a small quantity of oil floated to the surface. This was extracted with benzene, and shown to be methylaminothiophenol

(by oxidation to the disulfide with m.p. 68°). Upon further acidification, a voluminous precipitate of a pale yellow solid substance was formed. After treatment in water with animal charcoal and recrystallization it melted at 132°. It was in the form of small colorless leaves with a mercaptan odor. The oxygen of the air oxidized it more slowly than the previous mercaptans. The oxidation product was the disulfide, with m.p. 173-175°.

The compound was soluble in water, alcohol, and ether, slightly soluble in benzene and dichloroethane, insoluble in ligroin. It dissolved in caustic alkalies and in ammonia, as well as in concentrated mineral acids, from which it was reprecipitated unchanged upon dilution. The molecular weight, by Rast's method, calculated for $C_8H_9O_2NS$, was 185.

Found %: N 7.83.

$C_8H_9O_2NS$. Calculated %: N 7.65.

N-Benzyl-o-aminophenyl Mercaptan

20 g of Captax and 15 g of benzyl chloride were boiled for 4 hours with a reflux condenser. The dark tarry mass was recrystallized from 50 ml of benzene, washed well with benzene on the filter, and after removal of the solvent, ground in a mortar with a 10% solution of caustic soda. The product was washed with water, thoroughly squeezed out, and dried. It melted at 149-150°. Yield 18 g, or 58% of theory.

To the liquefied mixture of 25 g of caustic potash and 30 ml of water at 200°, there was added, with stirring, 13 g of benzylbenzothiazolethione. Then the temperature was raised to 230° and maintained at this level for 15 minutes. The melt was cooled, dissolved in water, and neutralized with hydrochloric acid. The oil which separated was extracted with benzene and distilled in vacuum. B.p. 179° at 30 mm. The product was in the form of light yellow leaves with m.p. 37°. Melting point of the disulfide 104°.

Found %: N 6.83.

$C_{13}H_{13}NS$. Calculated %: N 6.51.

N-Phenyl-o-aminophenyl Mercaptan

This was obtained according to the directions described by Kiprianov and Ushenko [5]. Yield of product, 72% of theory calculated on the basis of N-phenylbenzothiazolone. It was a pale yellow oil which crystallized upon standing. B.p. 175° at 8 mm.

SUMMARY

By the action of alcoholic alkali upon N-alkyl or N-aryl derivatives of benzothiazolone, benzothiazolethione, and benzothiazoloneimine, good yields of N-Methyl, N-ethyl, N-carboxymethyl, N-benzyl, and N-phenyl o-aminophenyl mercaptans were obtained. A method was developed for obtaining the first four compounds from Captax (technical 2-mercaptobenzothiazole). N-Alkyl and N-aryl aminothiophenols were found to be very reactive substances. In air, they oxidized to the disulfides. By suitable condensation, they were converted into quaternary salts of benzothiazole, and benzothiazine, and into derivatives of benzothiazoline.

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* See CB translation p. 1519 ff.



THE PREPARATION AND PROPERTIES OF BARIUM SALTS OF DINITRO-(1,5)- β -NAPHTHOLSULFONIC ACID-(2,7)

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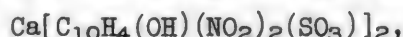
During the investigation of calcium and potassium salts of dinitro-(1,5)- β -naphtholsulfonic acid-(2,7) it was observed that barium formed two salts with the anion of dinitro- β -naphthosulfonic acid: 1) a yellow salt, formed in weakly acid and neutral solutions, and 2) a red salt, formed in alkaline solutions.

The purpose of the present work was to investigate the properties of the yellow and red salts of barium with dinitro-(1,5)- β -naphtholsulfonic acid-(2,7) and the conditions of their formation. According to the results of preliminary experiments [1], these salts were not very soluble (much less soluble than the calcium salt of dinitro- β -naphtholsulfonic acid). This gave some reason to suppose that the anion of dinitro-(1,5)- β -naphtholsulfonic acid might possibly be used for the detection of the barium ion in analytical chemistry.

As a starting material for the preparation of the barium salt, we used the calcium dinitro-(1,5)- β -naphtholsulfonate-(2,7), obtained from the technical sodium salt of β -naphtholsulfonic acid, the so-called F-acid salt, by the method of N.N.Vorozhtsov (senior). The method of preparation of the calcium salt of dinitro-(1,5)- β -naphtholsulfonic acid, in brief, consists of two steps:

First step, the preparation of the sodium salt of the F-acid, free from any admixture of the isomer, Schaeffer's 2,6-acid. Second step, the preparation of the 1,5-dinitro derivative and the preparation of the calcium salt.

The calcium salt of dinitro- β -naphtholsulfonic acid has the formula:



and crystallizes with 6 molecules of water.

The Properties and Conditions of Formation of the Yellow

Barium Dinitro-(1,5)- β -naphtholsulfonate-(2,7)

The yellow barium salt was precipitated in the form of yellow platelets with a rhombic shape by the action of a solution of barium chloride upon the neutral or weakly acid solution of the calcium salt of dinitro- β -naphtholsulfonic acid. The barium salt was filtered off, washed with cold water until the Cl^- was completely removed, and dried in the air. During the slow crystallization of the salt from hot solutions, crystals are obtained in the form of long platelets or thick needles; upon rapid crystallization from hot solutions, fine needlelike crystals are obtained, frequently stuck together in clumps.

The yellow barium salt formed several crystal hydrates. The yellow salt of barium, separated from solutions and dried in the air at a temperature of 100-110°, lost 12.39% of its weight, i.e., 6 molecules of H_2O . Dried at a temperature of 120-130°, it lost 14.16% of its weight, i.e., 7 molecules of H_2O . These figures were obtained not only by heating the crystalline salt, but also by the reverse

i.e., by dissolving a sample of anhydrous salt in water and evaporating the solution in air. Upon evaporating solutions of the yellow barium salt in a desiccator above CaCl_2 , a crystal hydrate was obtained with 8.62% of water, i.e., with 4 molecules of H_2O . Upon standing in the air and even in a desiccator above CaCl_2 , the anhydrous salt quickly gained weight as a result of the absorption of water.

The color of the anhydrous salt was orange-yellow. If aqueous solutions of the yellow salt were evaporated on the water bath, and there was very little salt in solution, all the salt obtained on evaporation had a red color. In case more concentrated solutions were evaporated, the red salt was obtained at the edges of the beaker, while at the bottom the red salt was covered in spots with the yellow salt. Upon repeated solution of the red and mixed salts in water, and evaporation of the water in air, the yellow crystalline salt was again obtained.

The determination of the quantity of barium in the yellow salt was carried out by the following method: a sample of the salt in a roasted porcelain crucible was treated with a small amount of concentrated H_2SO_4 . The salt quickly turned white because of the formation of BaSO_4 . The excess of H_2SO_4 was slowly driven off, and the charred residue was roasted to constant weight.

The amount of barium in the crystalline salt equalled 15.6%. The theoretical amount of barium in the different salts (in %) is

- 1) $\text{Ba}[\text{C}_{10}\text{H}_4(\text{OH})(\text{NO}_2)_2(\text{SO}_3)]_2 \cdot 7\text{H}_2\text{O}$ - 15.44.
- 2) $\text{Ba}[\text{C}_{10}\text{H}_4(\text{OH})(\text{NO}_2)_2(\text{SO}_3)]_2 \cdot 6\text{H}_2\text{O}$ - 15.76.
- 3) $\text{Ba}[\text{C}_{10}\text{H}_4(\text{OH})(\text{NO}_2)_2(\text{SO}_3)]_2$ - 17.99.

The solubility of the yellow barium salt was determined in the following manner: a hot concentrated solution of the salt was prepared and cooled to a definite temperature. The excess of salt precipitated out. After filtration, the saturated solution was evaporated on the water bath, and the beaker with the salt was dried to constant weight at 105-110°.

The solubility coefficient of the salt at 5° and at 9° was 0.1324 and 0.2695 g respectively. The salt was not very soluble in alcohol; it was very soluble in alkalis. Its solubility in dilute acids was of the same order as in water.

The Red Barium Salt of Dinitro-(1,5)- β -naphtholsulfonic Acid-(2,7)

Solutions of the yellow salts (ammonium, potassium, calcium) of dinitro- β -naphtholsulfonic acid, upon the addition of any alkali, become orange-colored or almost red. In addition, as we explained earlier [1], the yellow potassium and ammonium salts, which were difficultly soluble in water and weak acids, dissolved well in alkalis, and were not formed in alkaline solutions. We expressed the hypothesis that in alkaline solutions, the hydrogen of the phenol group was substituted by the metal ion, and the phenolate obtained was very soluble in water. Upon acidification, the red alkaline solution again became yellow, and a precipitate of the yellow salt (potassium, ammonium) again formed, i.e., the phenolate was decomposed by acids.

Barium, in alkaline solutions, formed with the anion of dinitro- β -naphtholsulfonic acid a clear red, slightly soluble salt; for its preparation we were able to use the yellow salt of calcium, potassium, or ammonium, adding BaCl_2 and a small quantity of any alkali (KOH , NaOH , $\text{Ba}(\text{OH})_2$, NH_4OH), or we could treat the solution

of the yellow barium salt with any alkali. From the point of view of purity of reagents, the most convenient method was the use of NH_4OH as an alkali.

To obtain the red salt of barium, we utilized the following methods:

1. To a solution of the calcium salt of dinitro- β -naphtholsulfonic acid, a solution of NH_4OH was added, and then a solution of BaCl_2 .
2. To a solution of the calcium salt BaCl_2 was first added, and then a solution of NH_4OH .
3. To a solution of the yellow barium salt of dinitro- β -naphtholsulfonic acid, a solution of NH_4OH was added.
4. To a solution of the ammonium salt of dinitro- β -naphtholsulfonic acid, a solution of NH_4OH was added, and then a solution of BaCl_2 .

In the first three cases, yellow crystals were first produced. These then turned red, and became overgrown with a mass of fine red needles. At the end of the process, there was obtained a very voluminous red precipitate, consisting of fine red needles which formed aggregates in the form of globules.

In the fourth case, when we started with the ammonium salt, which was only slightly soluble in water, no initial formation of yellow crystals was observed, but a precipitate was obtained with an orange tint. Only after lengthy standing of the solution with the precipitate, and repeated heating and cooling, and many washings, was the precipitate obtained with a clear red color.

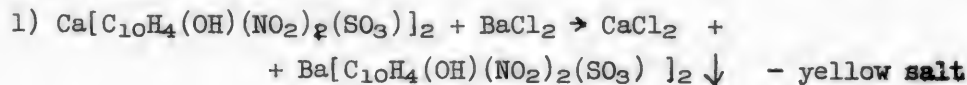
The formation of the red barium salt is very striking if the reaction is carried out on a slide and observed by means of a microscope. If a drop of BaCl_2 solution is added to a drop of calcium salt solution on the slide, yellow crystals are formed in the shape of long platelets, with 2 or 3 individual often gathered together in clumps. Upon treatment from above with gaseous NH_3 (by bringing close a small rod moistened with concentrated NH_4OH solution) the solution and crystals quickly turn red, and the crystals become covered with a mass of fine red needle-shaped crystals like a fleece. These quickly grow into fine needles, which branch considerably, and form a dense network of fine crystals, covering the crystals which were first formed. Thus, together with the yellow crystals, there is formed a spherical aggregate of fine red needles.

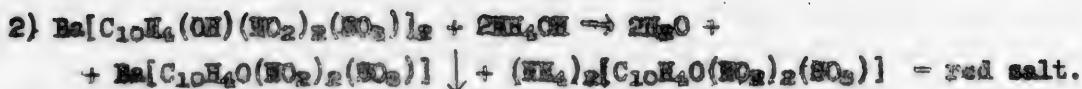
If we place a solution of the yellow barium salt on the microscope slide along with crystals of this salt and treat both from above with gaseous NH_3 , the same phenomenon is observed, i.e., the solution and crystals both turn red, and the latter are overgrown with red needles.

The amount of barium in the red salt was determined in the same way as in the yellow salt, i.e., by treatment of a sample of the salt with concentrated H_2SO_4 , and roasting of the BaSO_4 precipitate to constant weight.

When as the starting material for the preparation of the red barium salt the calcium salt or the yellow barium salt is used, the amount of barium in the red salt equalled 30.4 to 30.5%. In samples of the red salt utilized previously for the determination of solubility (with heating and cooling of the solution), the amount of barium found was somewhat lower (29.8 to 30.0%).

If we assume that in the red salt the barium takes the place of hydrogen in the sulfonic acid group and the phenol group, then the amount of barium must equal 30.54%, i.e. the reaction for the formation of the red barium salt may be represented in this way:





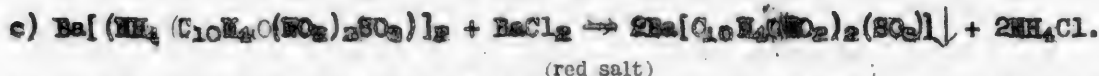
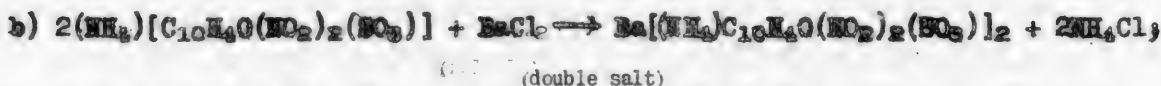
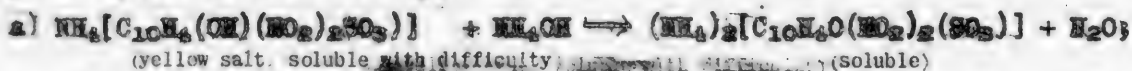
A molecule of the red barium salt of dinitro- β -naphtholsulfonic acid contains either 1 barium ion (substituent for hydrogen) in the sulfonic acid and phenyl groups) $\text{Ba}[\text{C}_{10}\text{H}_4\text{O}(\text{NO}_2)_2(\text{SO}_3)]$, or the molecule contains 2 barium ions, one of which is united to two sulfonic acid groups, the other to the oxygen of the phenol group, that is, the molecule of a double salt:



In case the red barium salt is prepared from the ammonium salt, the amount of barium found is somewhat lower, but the results are not the same for different samples.

The longer the red salt has stood unfiltered, and the greater the number of times the solution containing the salt has been heated and cooled, the closer to 30.5% is the amount of barium found in the salt. This gives us reason to suppose that the substitution of ammonium in the sulfonate group takes place with more difficulty, and the reaction proceeds more slowly, so that here a small amount of the double salt of ammonium and barium remains.

The reaction for the formation of the red barium salt from the ammonium salt may be represented in this way:



As we had observed previously [1] that the action of a BaCl_2 solution plus alkali in the difficultly soluble potassium salt leads to the formation of the double salt with the composition $\text{Ba}[(\text{K})\text{C}_{10}\text{H}_4\text{O}(\text{NO}_2)_2(\text{SO}_3)]_2$ (red color), we assumed that when the ammonium salt too was used as the starting material a double salt was also obtained. Both qualitative and quantitative tests were carried out for NH_4 . The qualitative tests were carried out by treating the red salt with HCl , then with an excess of NaOH . Upon heating, NH_3 was detected with a strip of paper which had been dipped in H_2SO_4 . The quantitative determination of NH_4 was carried out by microtitration [2].

The amount of NH_4 in different samples varied, but was always much lower than corresponded to the composition of the double salt of ammonium and barium. In samples of the red salt obtained after lengthy standing of the salt in solution, with repeated heating and cooling of the solution, and very lengthy washing, no ammonia at all was found. This confirmed the slowness of formation of the red barium salt from the yellow ammoniacal salt.

The red barium salt of dinitro- β -naphtholsulfonic acid contained no water of crystallization.

Determination of the Solubility of the Red Barium Salt of Dinitro-(1,5)- β -naphtholsulfonic Acid-(2,7)

A saturated solution of the salt was prepared by allowing the salt to stand in solution for a long time (2 to 3 weeks), with frequent shaking. The temperature was 17°. The saturated solution was evaporated on the water bath. The solubility

coefficient of the salt under these conditions corresponded to 0.033 g., that is, the solubility was lower than for the yellow salt of barium and the yellow salt of potassium (the solubility of the latter was 0.1003 at 15.3°[1]).

Quite different results were obtained if the saturated solution of the red salt was prepared by boiling it with the solution, followed by cooling to the given temperature to precipitate the excess of salt from the solution. The solubility coefficient of the salt, determined by this method, equalled: 0.2865 g at 9°, 0.3235 at 18°, 0.3310 at 20°, i.e., almost 10 times as great as in the first determination (preparation of the saturated solution without heating). The solubility of the red salt was found to be higher not only than the solubility of the yellow potassium salt, but also than that of the yellow barium salt; this was in contradiction to the experiments in which a voluminous precipitate of the red salt was obtained from solutions of the yellow barium salt in the presence of alkali. In addition, it was noted that the cold solution of the red barium salt had a yellow-orange color, but turned red, almost cherry-colored, upon heating, and became yellow-orange again upon cooling. The solution of the salt took place much more slowly upon heating, and required lengthy boiling, or else there was no precipitation of the salt when the solution was cooled. In this case, it was impossible to consider the cold solution as supersaturated, as no precipitate was observed if the solid salt was added to the solution.

These facts give us reason to suppose that boiling resulted in hydrolysis of the red salt, and that the products of hydrolysis were more soluble than the original salt.

If for the red salt we assume the formula $\text{Ba}_2[\text{C}_{10}\text{H}_4\text{O}(\text{NO}_2)_2(\text{SO}_3)]_2$ (Fig. 1), it is here possible to assume the addition of hydroxyl to the barium which is attached to two phenol groups; the bond to one of these breaks, and a hydrogen ion adds on to the oxygen of the phenol group. Then the molecule of the hydrolyzed salt may have the structure (Fig. 2).

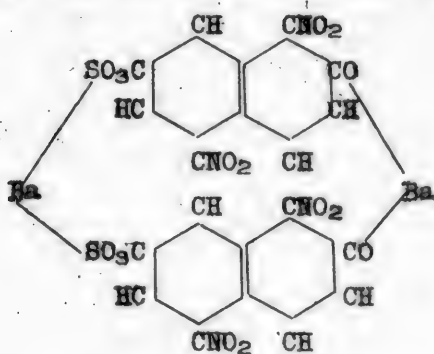


Fig. 1

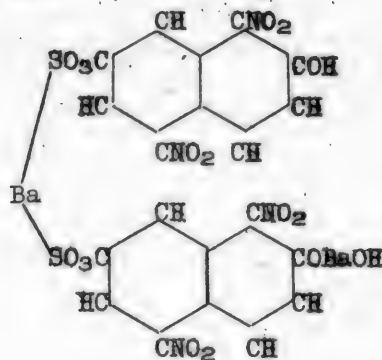
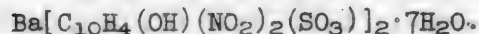
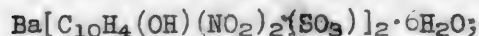
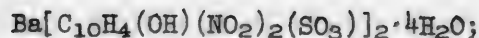


Fig. 2

The amount of barium in this salt corresponds to 29.96%. The presence of products of hydrolysis may explain the lowering of the results in the determination of the amount of barium in samples of the red salt, taken after the determination of solubility from heated solutions.

SUMMARY

1. The yellow barium salt of dinitro-(1,5)- β -naphtholsulfonic acid-(2,7) is formed in neutral or weakly acid solutions. It has the formula $\text{Ba}[\text{C}_{10}\text{H}_4(\text{OH})(\text{NO}_2)_2(\text{SO}_3)]_2$ and gives the crystal hydrates:



The solubility coefficient in water is 0.2695 g at 19°.

2. The red barium salt of dinitro-(1,5)- β -naphthosulfonic acid is obtained from alkaline solutions of the yellow salts of calcium or ammonium by the addition of BaCl_2 , or from the yellow barium salt. The amount of barium in it is 30.45%. This corresponds to the formula $\text{Ba}[\text{C}_{10}\text{H}_4(\text{NO}_2)_2(\text{SO}_3)]_2$ or $\text{Ba}_2[\text{C}_{10}\text{H}_4\text{O}(\text{NO}_2)_2(\text{SO}_3)]_2$.

In the formation of the red barium salt from the yellow ammonium salt of dinitro-(1,5)- β -naphtholsulfonic acid, the reaction takes place slowly. The barium-ammonium double salt is obtained as an intermediate product.

3. The red salt does not form crystal hydrates. Boiling the aqueous solutions of the salt results in its hydrolysis. The products of hydrolysis are more soluble than the original salt. For solubility determinations, it is impossible to use solutions which have been boiled or heated for a long time. The solubility coefficient at 17° (in unheated solutions) is 0.033 g, which corresponds to 0.1008 g of barium per liter, or $0.73 \cdot 10^{-3}$ g-ion of barium per liter.

4. It is possible to use the formation of the red barium salt for the detection of barium ions.

However, the solubility of the red barium salt is greater than the solubility of BaSO_4 , and therefore it can scarcely be considered to have wide applicability in analytical chemistry.

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- [2] I.M.Korenman, Quantitative Microchemical Analysis, 1930, p 03.

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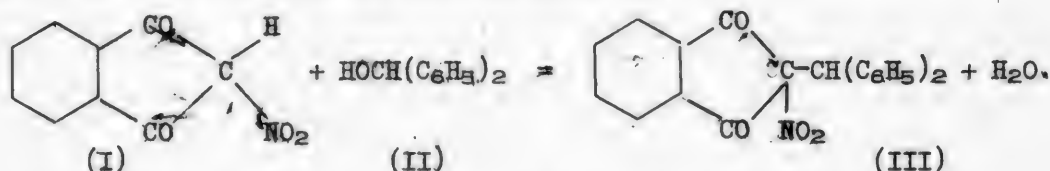
THE CONDENSATION OF 2-NITROINDANEDIONE-1,3 WITH BENZOHYDROL

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If an aqueous solution of 2-nitroindanedione-1,3 (I) is heated together with benzohydrol (II), the latter (m.p. 68°) melts and floats on the liquid as an oil insoluble in water. The oil, however, soon solidifies. As can be seen, the reaction between the two components takes place very easily. It was of interest to pursue the study of this reaction further.

As is known, the hydroxyl group in benzohydrol is a very active one, and benzohydrol easily condenses with compounds containing active hydrogen, like, for example, acetoacetic ester [1]. As nitroindanedione also has an active hydrogen atom, we had reason to expect that here too a similar reaction would take place, with the formation of 2-nitro-2-benzohydrolindanedione-1,3 (III).



For the preparation of a pure product, condensation in an aqueous medium appeared not quite suitable, for the condensation product (III) contained in addition unreacted benzohydrol. After purification by crystallization from alcohol, approximately 30 to 40% of the theoretical amount of pure product was obtained; therefore, we tried condensation in a single medium, particularly in alcohol, in which both components were very soluble. The crystalline reaction product was obtained almost pure. However, even in this case, the yields were no better, especially because of the fact that a side reaction took place at the same time. As is known, a solution of benzohydrol in ethyl alcohol even at room temperature [2] in the presence of sulfuric acid, or upon heating in the presence of hydrochloric acid [3] is transformed into ethylbenzohydryl ether (IV). As the nitroindanedione is strongly acid [4], it is not difficult to understand that in its presence the formation of this ether easily takes place.

The most suitable medium for the condensation of nitroindanedione with benzohydrol appeared to be glacial acetic acid. It was enough to boil this for 5-10 minutes. More lengthy boiling not only did not increase the yields, but even lowered them. The best yields were obtained with molar ratios of the compounds in concentrated solution. The condensation product separated upon cooling in almost pure crystalline form in a yield 84% of theory. Various results of condensation experiments are given in the following table.

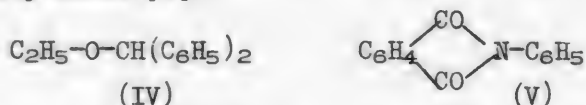
The nitrobenzohydrylindanedione (III) obtained crystallized in white prismatic needles, with m.p. 202°. It was fairly soluble in many organic solvents, especially upon heating. For example, it dissolved in ether, acetone, chloroform,

The Condensation of Nitroindanedione with Benzohydrol

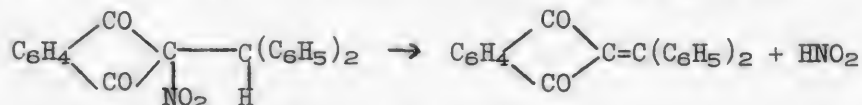
Amount of nitroindanedione, g	Molar ratio of nitroindanedione: benzohydrol	Amount of solvent, ml	Duration of heating (Min)	Yield of crystalline product (% of theory)
		Water		
1.15	1 :1	25	30	42.5
1.15	1 :1.5	70	30	37.1
1.73	1.5:1	25	30	30.7
2.3	2 :1.5	30	30	38.6
		ethanol		
1.15	1 :1	10	30	34.8
1.15	1 :1	10	10	30.4
1.15	1 :1	20	20	20.4
		Glacial acetic acid		
1.15	1 :1	30	120	47.0
1.15	1 :1.5	30	60	55.6
1.4	1.2:1	30	60	34.6
1.7	1.5:1	30	30	44.8
1.4	1.2:1	20	15	65.9
1.4	1.2:1	20	10	73.7
1.27	1.1:1	20	10	72.0
1.15	1 :1	15	10	84.4

benzene, glacial acetic acid, nitrobenzene, pyridine, and aniline. In ethanol, its solubility was small even upon heating (a saturated solution contained approximately 0.4% of the compound). It dissolved somewhat better in amyl alcohol.

The condensation product did not decolorize bromine water or potassium permanganate. The attempts to brominate the dry compound or its solution in carbon tetrachloride or glacial acetic acid were unsuccessful. The action of concentrated or fuming nitric acid did not result in nitration. Attempts to prepare the oxime or phenylhydrazone were also unsuccessful; however, this had been frequently noted for ketones of a five-membered ring. Upon heating the compound with aniline in glacial acetic acid, the phthalanil (V) was obtained. The formation of the phthalanil by the action of aniline upon indanedione derivatives has been previously noted [5].

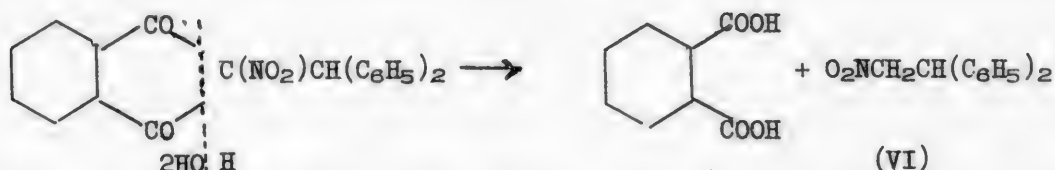


When the dry substance was carefully heated in a test tube, it melted, and was changed into a deep yellow liquid, which on further heating decomposed, emitting brown vapors. If a damp glass rod was held in them, and the drop of solution was then mixed with diphenylamine in concentrated sulfuric acid, a blue color was obtained. Nitrobenzohydrylindanedione dissolved in concentrated sulfuric acid upon heating to give an orange color. As the temperature was increased, the color darkened. If this dark brown solution was poured into water, a violet solution was obtained. This solution decolorized bromine water and a solution of permanganate; therefore, it contained an unsaturated compound. It is probable that under the action of the sulfuric acid, nitrous acid split off:

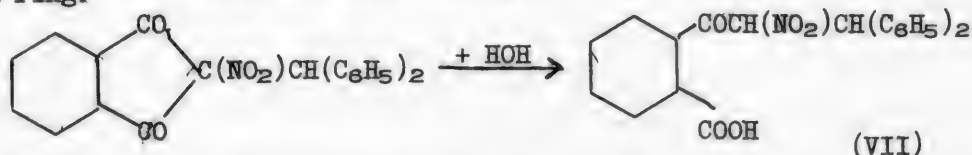


Unsuccessful attempts were made to extract the violet substance from aqueous solution. It is possible that sulfonation took place at the same time, and that the solution contained sulfonic acids of the compound.

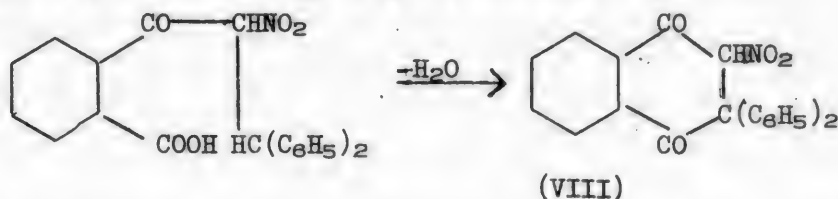
When the nitrobenzohydrylindanedione was boiled with caustic soda in aqueous or alcoholic solution, phthalic acid split off, and the corresponding nitro compound was obtained - benzohydrylnitromethane, or β,β -diphenyl- α -nitroethane (VI):



Upon less lengthy treatment with alkali, intermediate cleavage products were obtained, as a result of the breaking of only a single bond of the five-membered ring:



The acid formed separated out in the form of a curdy precipitate upon acidification of the alkaline solution; this precipitate still contained a great deal of water. After recrystallization from alcohol or ether, it melted at 123-124°. However, the crystals obtained were no longer soluble in ammonia and in cold dilute caustic alkali; this indicated that they were no longer the acid. The unrecrystallized acid dissolved in an excess of ammonia to give a yellowish solution, but when this solution was concentrated, there separated out white crystals with m.p. 123°, which were no longer soluble in ammonia. Consequently, the free acid is unstable, easily loses water, and, apparently, is changed to a new compound with the closing of a six-membered ring:



This widening of the five-membered ring into a six-membered one has been noted before [6] in the indanedione group. The correctness of formula (VIII), of course, still requires more detailed demonstration. In the meantime, we can only point out that upon treatment of compound (VIII) with an excess of alkali, it also, like nitrobenzohydrylindanedione, is cleaved into phthalic acid and benzohydrylnitromethane; this indicates that it has kept the same structural elements as the latter.

The extremely easy condensation of nitroindanedione with benzohydrol and the easy splitting off of phthalic acid from the condensation product permitted us, in the final result, to substitute the hydroxyl group in benzohydrol by the nitromethyl group:



Further investigation will show whether this is only a single particular case or a method that may have more general application.

Diphenylnitroethane is structurally similar to the insecticide DDT and in fact, according to the latest data [8], diphenylnitroethane and its derivatives possess insecticidal properties.

EXPERIMENTAL

The Condensation of 2-Nitroindanedione-1,3 with Benzohydrol

In Aqueous Solution. 1.15 g of nitroindanedione was dissolved in 25 ml of water and 0.92 g of benzohydrol was added. The mixture was boiled for a half hour with a reflux condenser. Upon cooling, the precipitate was filtered off with suction, washed with water, and dried. Yield, 1.2 g. After crystallization from alcohol, 0.77 g of nitrobenzohydrylindanedione (III) was obtained, or 42.5% of the theoretical. M.p. 198-200°.

In Alcoholic Solution. 1.15 g of nitroindanedione, 0.92 g of benzohydrol, and 10 ml of alcohol were boiled with a reflux condenser. The precipitate began to form after 20 minutes. After some time, the precipitate was filtered off, and the filtrate boiled again. The collected precipitates weighed 0.63 g, or 34.8% of the theoretical. M.p. 198-199°. Upon dilution of the filtrate with water, a thick odorless oil separated at the bottom. In its properties it was completely similar to the ethylbenzohydryl ether (IV) which is described in the literature.

In a Solution of Glacial Acetic Acid. 1.15 g of nitroindanedione, 0.92 g. of benzohydrol, and 15 ml of glacial acetic acid were boiled with a reflux condenser for 5 minutes. Upon cooling, white shining crystals of nitrobenzohydrylindanedione (III) precipitated out in the form of prismatic needles. Yield 1.53 g, or 84.4% of the theoretical. M.p. 202°.

0.786 mg substance: 0.358 ml N_2 (12°, 757 mm).

0.1374 g substance: 5.00 ml N_2 (20°, 751 mm).

Found %: N 4.36, 4.19.

$\text{C}_{22}\text{H}_{15}\text{O}_4\text{N}$. Calculated % N 3.92.

A determination of the molecular weight by Rast's method did not give good results, as the compound decomposed during the determination. The small tube filled with yellow gas, and the depression of the temperature kept on increasing. An ebullioscopic determination in acetone was carried out without difficulty: 0.4157 g of compound, 19.28 g of acetone, increase of b.p. 1.03°.

Found %: M 356.0.

$\text{C}_{22}\text{H}_{15}\text{O}_4$. Calculated %: M 357.1.

Nitrobenzohydrylindanedione was boiled for several hours with moderately concentrated sulfuric acid. The compound did not dissolve; it only turned rose color without difficulty. After recrystallization, the residue appeared to be the unchanged compound (m.p. 198°). The sulfuric acid filtrate, with resorcinol, gave the fluorescein reaction. Upon heating with concentrated sulfuric acid, nitrobenzohydrylindanedione undergoes charring. The filtrate gives the fluorescein reaction.

The Cleavage of Nitrobenzohydrylindanedione by Aniline

1.2 g of nitrobenzohydrylindanedione was dissolved in 50 ml of glacial acetic acid, and 2 g of freshly distilled aniline was added. The mixture was boiled with a reflux condenser for 3 hours. Upon cooling and standing, large

needle-shaped crystals of phthalanil (V) separated out of the brown solution, approximately 1 g in amount. They were filtered with suction, washed with glacial acetic acid, and recrystallized from alcohol to which activated carbon had been added. The crystals were white, and had m.p. 206-207°. Upon mixing with pure phthalanil, no depression of the melting point was observed.

5.612 mg substance: 0.300 ml N₂ (17°, 762 mm).

Found %: N 6.31

C₁₄H₉O₂N. Calculated %: N 6.28.

The Cleavage of Nitrobenzohydrylindanedione by Alkali

Sodium Methylate. 1) 3 g of nitrobenzohydrylindanedione was added to 30 ml of a 1.5% sodium methylate solution. The nitrobenzohydrylindanedione immediately dissolved with a yellow color. The solution was diluted with 60 ml of water, the slight cloudiness was filtered off, and hydrochloric acid was added. The solution was decolorized and a curdy precipitate formed. After drying in the dessicator, 3.1 g of compound (VII) was obtained. For purposes of purification, it was recrystallized from alcohol; rectangular platelets of 2-nitro-3,3-diphenyl-2,3-dihydro- α -naphthoquinone (VIII) were obtained. The alcoholic filtrate was diluted with water, and to the milky-white liquid obtained, a small amount of concentrated hydrochloric acid was added. A precipitate gradually formed. It was a mixture of crystals with amorphous material. After mechanically washing out the amorphous material, a few crystals remained, in the form of long needles with m.p. 69°. However, these were not benzohydrol, for a mixture with pure benzohydrol (m.p. 68°) melted at 49.51°.

For purposes of analysis, the 2-nitro-3,3-diphenyl-2,3-dihydro- α -naphthoquinone was recrystallized once more from alcohol. M.p. 123-124°.

11.914 mg substance: 0.402 ml N₂ (13°, 749 mm).

10.186 mg substance: 0.329 ml N₂ (14°, 755 mm).

Found %: N 3.97, 3.82.

C₂₂H₁₅O₄N. Calculated %: N 3.92.

Compound (VII) was dissolved in an excess of ammonia and the light yellowish solution was carefully evaporated. A white precipitate formed. This was filtered off and the filtrate evaporated to dryness. Both substances obtained were the same. They were no longer soluble in ammonia, and melted at 120-122°; after recrystallization from alcohol, the m.p. was 123-124° (VIII).

2-Nitro-3,3-diphenyl-2,3-dihydro- α -naphthoquinone dissolved in ether, alcohol, acetone, benzene, chloroform, pyridine, and glacial acetic acid. It also dissolved slowly in concentrated sulfuric acid in the cold, the solution taking on a deep yellow color. Upon heating, the color darkened. It also dissolved in caustic soda, giving dark yellow solutions. By treatment with sodium methylate and ether, the sodium salt could be isolated in dry form.

To 0.5 g of 2-nitro-3,3-diphenyl-2,3-dihydro- α -naphthoquinone there was gradually added, with gentle heating, a freshly prepared 5% solution of sodium methylate, until solution was complete. Then 5 ml of ether was added, and the mixture allowed to stand until the following day.

There were thus obtained 0.322 g of the sodium salt in the form of small yellow needles.

0.500 g substance: 0.0420 g Na₂SO₄

Found %: Na 5.96.

C₂₂H₁₄O₄NNa. Calculated %: Na 6.07.

The sodium salt was very soluble in water. Upon acidification, a white

precipitate was obtained. After crystallization from alcohol, it had m.p. 124°. It gave no m.p. depression when mixed with the original product.

Upon careful heating in a small test tube, the compound melted, forming a colorless liquid, which solidified upon cooling to give a transparent, vitreous mass. Upon heating above the melting point, the compound took on a yellow color, and then decomposed vigorously, with the evolution of gas.

a) 4 g of nitrobenzohydrylindanedione was added to 40 ml of a 5% sodium methylate solution and boiled for 4 hours. At first the liquid was yellow; then it turned orange, and finally brown-red. The liquid was diluted with twice the amount of water and 7 or 8 ml of concentrated hydrochloric acid was added to the intensely colored solution. A soft, yellow-orange tarry mass separated out. It was washed with water and dried, and the approximately 4 g of material obtained was dissolved in 20 ml of alcohol. From the solution there precipitated out a small quantity of a white precipitate of 2-nitro-3,3-diphenyl-2,3-dihydro- α -naphthoquinone (VIII), with m.p. 123°. The alcoholic filtrate was diluted with water and 8 ml of concentrated hydrochloric acid added; an orange oily substance precipitated out, which weighed about 6 g in unpurified form. Part of the substance was dissolved in a very small amount of alcohol (for example, 4 g in 5 ml of alcohol) and allowed to stand in order to crystallize. The crystallization of benzohydrylnitromethane (VI) took place very slowly. The addition of a drop of concentrated hydrochloric acid speeded up the crystallization slightly. Light yellow crystals were obtained, with m.p. 68-70°. The remainder of the oily material was distilled with steam. The distillate, containing oily drops, was extracted with ether, and the ethereal solution dried over anhydrous sodium sulfate; the ether was then driven off. A light yellow oily residue remained; this was dissolved in a very small amount of alcohol, from which upon standing, there separated out large white crystals of benzohydrylnitromethane, with m.p. 70-71°.

6.200 mg substance: 0.296 ml H_2 (13°, 766 mm).

9.271 mg substance: 0.463 ml H_2 (13°, 767 mm).

Found %: N 5.74, 6.02.

$C_{14}H_{13}O_2$ Calculated %: N 6.17.

Caustic Soda. 4 g of nitrobenzohydrylindanedione was heated in 20 ml of a 5% aqueous solution of caustic soda until it was completely dissolved. The solution was then diluted with twice the amount of water and concentrated hydrochloric acid was added until the solution was decolorized. A total of approximately 7 ml was needed. The tarry precipitate (4 g) which formed was dissolved in 5 ml of alcohol with gentle heating, and filtered. Upon standing, a white crystalline precipitate of benzohydrylnitromethane slowly formed. It was filtered off with suction, and carefully washed with a very small amount of alcohol. 2.25 g of light yellowish crystals was obtained. After repeated crystallization from alcohol, the m.p. was 70°.

The aqueous solution was acidified and the tarry precipitate filtered off; the solution was then extracted with ether. After evaporation of the ether, the residue was sublimed. White needles of phthalic anhydride were obtained, with m.p. 128°. A mixture with pure phthalic anhydride gave no depression of the melting point. With resorcinol and concentrated sulfuric acid, it gave the fluorescein reaction.

Benzohydrylnitromethane did not dissolve in cold water. Upon heating, it melted, and upon cooling, it floated in the water in the form of an oily drop. It dissolved very easily in alcohol. It likewise dissolved easily in benzene, ether, acetone, and other organic solvents. It dissolved with great difficulty in naphtha. Rapid crystallization from alcohol gave needles, slow crystallization gave large many-faced crystals (octahedra).

A solution of benzohydrylnitromethane in glacial acetic acid, upon reduction with zinc dust, gave with bindone an intense violet color [7]; this indicated that the benzohydrylnitromethane was easily reduced to the corresponding amino compound, whereas nitrobenzohydrylindanedione and 2-nitro-3,3-diphenyl-2,3-dihydro- α -naphthoquinone did not give this reaction, their nitro groups splitting off upon reduction, as has often been found to happen with aliphatic nitro compounds.

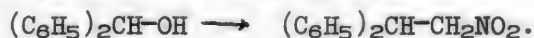
SUMMARY

1. The condensation of 2-nitroindanedione with benzohydrol gives 2-nitro-2-benzohydrylindanedione-1,3.

2. Upon brief treatment with alkali, 2-nitro-2-benzohydrylindanedione-1,3 isomerizes to give 2-nitro-3,3-diphenyl-2,3-dihydro- α -naphthoquinone.

3. Upon more energetic treatment with alkali, 2-nitro-2-benzohydrylindanedione-1,3 splits off phthalic acid and gives benzohydrylnitromethane.

4. The overall result of the reaction is the substitution of the hydroxyl group of benzohydrol by the nitromethyl group:



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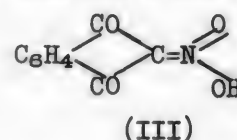
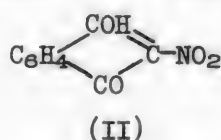
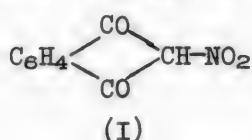


THE STRUCTURE OF 2-NITROINDANEDIONE-1,3 AND ITS SALTS

G. Ya. Wanag and E. Yu. Gudrinietse

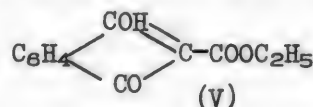
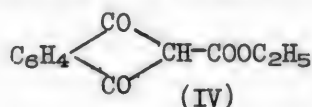
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2-Nitroindanedione-1,3 [1] can exist theoretically in three forms: as the nitrodiketone (I), as the nitroketoenol (II), and as the diketonitronic acid (III):



Nitroindanedione is very soluble in water and in alcohol, but does not dissolve in ether. The aqueous solutions show a strongly acid reaction; a determination of the pH shows that nitroindanedione equals hydrochloric acid in its acid properties. With regard to the structure of the nitroketones, Hantzsch is of the opinion [2] that they most probably exist as ketonitronic acids, while Meyer [3] assumes that the nitroenol form is the most probable, as the nitro group is much slower to enolize than the carbonyl group. The same views are held by Arndt and Rose [4], who point out that the nitro group acts only in the role of "conjugation partner".

Several indications about the possible structure of nitroindanedione in solution are given by comparison with the ethyl ester of indanedionecarboxylic acid (IV), which, according to Hantzsch [5], exists, both in the form of salts as well as in the free form, almost entirely as the enol. These investigations, carried out some time back by one of us together with Bungs [6], led to the conclusion that nitroindanedione isomerizes chiefly into the ketonitronic acid (III).



It was of further interest to compare the properties of the salts of nitroindanedione with the salts of the ethyl ester of indanedionecarboxylic acid. In addition to having theoretical interest, this may also have some practical value. It is known that nitroindanedione shows several valuable analytical properties, giving characteristic precipitates or colors both with various inorganic cations [1] as well as with organic bases. Because of this, they can be used for isolation, identification, and separation [7 8 9 10]. It was of interest to make clear whether the more accessible ester of indanedionecarboxylic acid (IV), which has a similar structure, showed the same valuable properties.

Several salts of the ethyl ester of indanedionecarboxylic acid had previously been prepared by Hantzsch [11], who precipitated them from hot aqueous solutions, as well as from anhydrous solutions. We systematically investigated the precipitation from cold aqueous solutions of inorganic salts with a solution of the sodium

salt of the ethyl ester of indanedionecarboxylic acid, in the same way as the investigation with nitroindanedione [7,8] had previously been carried out. The salts of the ethyl ester of indanedionecarboxylic acid appeared in general to have little solubility in water, but seldom precipitated in crystalline form. They were usually obtained as indefinitely crystalline, amorphous, or gelatinous precipitates, showing no particularly valuable properties for analytical purposes. Inorganic bases, with a number of which nitroindanedione gives particularly insoluble precipitates, either gave no precipitate at all with the sodium salt of the ethyl ester of indanedionecarboxylic acid, or gave one only at comparatively high concentration. Thus, the two reagents behave in completely different ways, from which it follows that their structures too must be different.

Both reagents dissolve in water to give a yellow color, and most of their salts are also colored yellow. The mercury and iron salts were of especial interest. Both the monovalent and bivalent mercury salts of the ethyl ester of indanedionecarboxylic acid had a white color; this indicated that they were structurally different from the other salts. Hantzsch showed [12] that with keto-enols, where there was a choice, mercury attached itself by preference to the carbon, rather than to the oxygen atom; consequently, these mercury salts are derivatives of form (IV), and all the others of form (V). The mercury salts of nitroindanedione are yellow, like all the other salts of this compound; consequently, they are not derivatives of the keto-enol form, but of form (III).

Ferric chloride gives with the ethyl ester of indanedionecarboxylic acid a red color. This indicates the presence of enol hydrogen. Nitroindanedione gives no color at all with ferric chloride. Especially characteristic are the salts of bivalent iron. As has been previously described [1], the nitroindanedione salt of bivalent iron crystallizes in violet-black hexagonal tablets, and differs from all the other salts of nitroindanedione. The salt has little solubility in water, but is somewhat soluble in various organic solvents; for example, it can be recrystallized from amyl alcohol. The salt of bivalent iron with the ester of indanedionecarboxylic acid was also almost insoluble in water and crystallized in red-brown hexagonal tablets. This salt was also soluble in several organic solvents, and could also, by way of example, be recrystallized from amyl alcohol. Analysis showed that this salt had a normal composition.

0.5620 g salt (dried at 110°): 0.0874 g Fe_2O_3 .

Found %: Fe 10.83

$\text{C}_{24}\text{H}_{18}\text{O}_8\text{Fe}$. Calculated %: Fe 11.40.

Thus, both salts are similar, but as the salt of the ethyl ester of indanedionecarboxylic acid can be a derivative of only the enol form, it follows that the ferrous salt of nitroindanedione, in contradistinction to all the other salts, is also a derivative of its enol form (II). When the violet solutions of this salt are heated, they turn yellow, and the violet salt can no longer be obtained from them. Therefore, the enol form is unstable, and upon heating goes over into the more stable form of ketonitronic acid.

Several salts of nitroindanedione when in the dry form have only a slight yellowish color [7,8], and the remaining salts could be obtained even completely white. These must be considered as derivatives of the nitroketone (I). In water, however, these salts dissolved to give a yellow color. This indicates that they were again transformed into the ketonitronic acid form.

SUMMARY

From a comparison of the properties of the salts of nitroindanedione and of the ethyl ester of indanedionecarboxylic acid it follows that in an aqueous solution of the nitroindanedione the chief form is the ketonitronic acid. Most of the salts of nitroindanedione have the same structure. The salt of bivalent

of nitroindanedione are derivatives of the nitroketone form.

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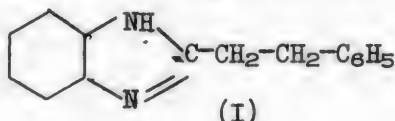
INVESTIGATIONS IN THE FIELD OF IMIDAZOLE DERIVATIVES

II. THE SYNTHESIS OF SEVERAL NEW PHENYL AND ALKYPHENYL DERIVATIVES OF BENZIMIDAZOLE

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As we have previously shown [1], upon heating in hydrochloric acid medium at 180° under pressure, o-phenylenediamine condenses smoothly with carboxylic acids, forming the corresponding 2-substituted derivatives of benzimidazole. In this manner, we obtained, in almost theoretical yield, 2-phenyl-2-benzyl and other derivatives of benzimidazole, including 2-(β-phenylethyl)-benzimidazole (I), which is described in the present communication:



We assume that under the conditions indicated above, the formation of benzimidazole derivatives takes place by steps involving intermediate products, these are obtained as a result of the introduction of an unshared electron pair of one of the amino groups of the o-diamine into the electron-lacking cation of

the carboxylic acid $\text{R}-\text{C}^+\begin{matrix} \text{OH} \\ \text{OH} \end{matrix}$, the latter is formed as a result of the presence of hydrogen ions in the solution.

The successful course of this first stage of the reaction, obviously, must depend, on one side, on the properties of the given carboxylic acid - on the ease with which under the given conditions it is able to add a proton to form the active cation. On the other side, it depends on the properties of the given o-diamine - on its basicity. As we have already shown [1], the free o-diamine takes part in the reaction, as it is always present in aqueous acid solutions along with the salt; it is obvious that the more basic the amine, the lower its concentration in acid solutions, and the greater the concentration of its salts in such solutions. However, the more basic amines are easily acylated by carboxylic acids.

Thus, the basic quality of the amine must have a dual effect on the course of the condensation in hydrochloric acid medium.

It therefore appeared of interest to investigate the reactions, not only of o-phenylenediamine but of other o-diamines of the benzene series, as well, with

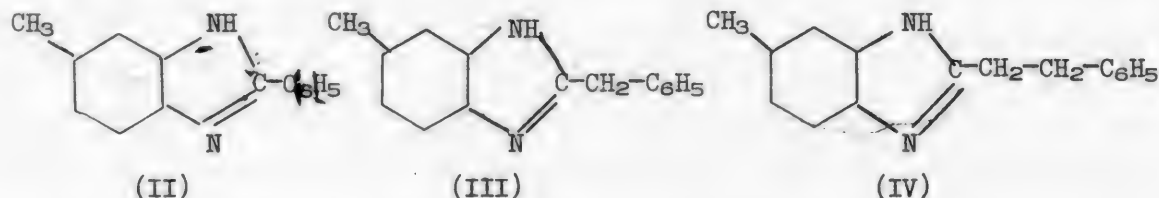
In order to confirm the structure we obtained this compound (I) by hydrogenating 2-styrylbenzimidazole, which had been formed by the condensation of 2-methylbenzimidazole with benzaldehyde.

**We intend to take up the study of this side of the reaction later on.

carboxylic acids in the presence of hydrochloric acid.

First of all, 3,4-toluylenediamine was chosen for investigation. As is known, this has somewhat stronger basic (electron-donor) properties than o-phenylenediamine. Its condensation with benzoic acid in the presence of hydrochloric acid gives 2-phenyl-5-methylbenzimidazole (II), which was synthesized for the first time by Ginzberg [2]. The yield of this compound, just as of o-phenylenediamine, for a definite temperature and a definite reaction time, depends on the concentration of hydrochloric acid used. At first, as the concentration of hydrochloric acid is increased to 20%, the yield of condensation product increases. Then, upon further increase of the concentration of hydrochloric acid, it falls sharply. However, at the point of optimal concentration of hydrochloric acid, where o-phenylenediamine condenses quantitatively with benzoic acid, 3,4-toluylenediamine gives only a 53% yield of 2-phenyl-5-methylbenzimidazole (II)*. We must note also that in 35% hydrochloric acid 3,4-toluylenediamine condenses in all only to the extent of 3%, while at the same time o-phenylenediamine condenses under these conditions to 48%. On the other hand, in 10% hydrochloric acid, the yield of condensation product from 3,4-toluylenediamine exceeds the yield of product from o-phenylenediamine.

A similar picture is obtained when the condensation of 3,4-toluylenediamine is carried out with both phenylacetic acid, to give the previously undescribed 2-benzyl-5-methylbenzimidazole (III), and with β -phenylpropionic acid, leading to the formation of 2-(β -phenylethyl)-5-methylbenzimidazole (IV), which has also been unknown up to the present:



The yield of these compounds, under uniform conditions for carrying out the reaction, also appeared to be lower than for compounds from o-phenylenediamine and the same acids.

Thus, theoretical consequences, resulting from the mechanism of formation we suggested for benzimidazole derivatives, are completely confirmed for 3,4-toluylenediamine. Under conditions favoring the hydrolysis of its salts, this compound condenses more easily than the less basic o-phenylenediamine. On the other hand, under conditions which make hydrolysis more difficult, 3,4-toluylenediamine condenses with much more difficulty than o-phenylenediamine.

However, the low yield of the benzimidazole derivative of 3,4-toluylenediamine in comparison with that from o-phenylenediamine in hydrochloric acid of the optimal concentration is not to be explained only by the difficulty of hydrolysis of its salts.

The increase in basicity of the amine results in a strengthening of its tendency to react with oxidizing agents, and this leads to a side reaction in which azine dyes are formed, naturally decreasing the yield of benzimidazole derivative.

Even in the case of o-phenylenediamine, this side reaction has been clearly observed. It takes place to a much greater extent in the case of 3,4-toluylene-

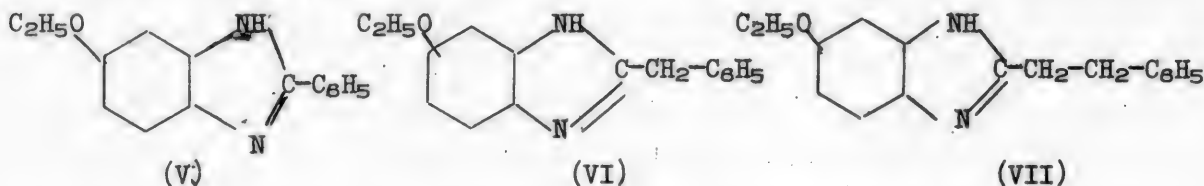
* A somewhat increased yield of this product may still be obtained if the condensation is carried out at a higher temperature (cf. experimental part.)

diamine, and the benzimidazole derivative is always obtained strongly contaminated with an admixture of blue dye. But this side reaction is expressed with especial force when more active substituents, like ethoxy and methoxy groups, are introduced into the o-phenylenediamine molecule.

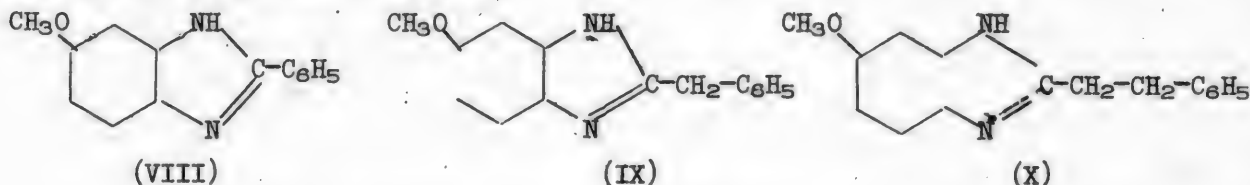
3,4-Diaminophenetole, and especially, 3,4-diaminoanisole have a very great tendency to oxidize. It is probable, therefore, that 3,4-diaminoanisole was obtained for the first time only in 1940 [3], as its purification and its constants have not been reported. We obtained it from nitroanisidine by reduction with hydrogen in the presence of nickel, according to the method of Regnault. Although it was twice distilled in vacuum, the 3,4-diaminoanisole none the less quickly turned black even upon storage in a sealed ampoule.

Therefore, in the condensation of 3,4-diaminophenetole and 3,4-diaminoanisole with carboxylic acids in hydrochloric acid solution, we did not succeed in obtaining the corresponding benzimidazole derivatives. Oxidation of these diamines took place more quickly than their condensation, which was made more difficult by the increased stability of their salts toward hydrolysis.

Only by melting equimolecular quantities of 3,4-diaminophenetole with benzoic, phenylacetic, and phenylpropionic acids at 180°, in tubes from which the air had been exhausted, did we obtain respectively 2-phenyl-5-ethoxybenzimidazole (V), 2-benzyl-5-ethoxybenzimidazole (VI), and 2-(β-phenylethyl)-5-ethoxybenzimidazole (VII) in 50 to 60% yield:

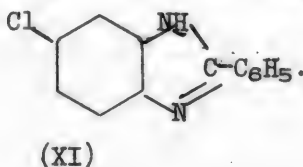


With 3,4-diaminoanisole and carboxylic acids, the same method gave 2-phenyl-5-methoxybenzimidazole (VIII), 2-benzyl-5-methoxybenzimidazole (IX), and 2-(β-phenylethyl)-5-methoxybenzimidazole (X):



Along with the o-diamines which were more basic than o-phenylenediamine, it appeared of interest to investigate the condensation with carboxylic acids of the less basic amines. Of the latter, we chose 3,4-diaminochlorobenzene.

As in the preceding cases, the condensation of this diamine with benzoic acid in hydrochloric acid was carried out at different concentrations of the latter. We thus observed that with an increase in the concentration of the hydrochloric acid up to 25%, the yield of 2-phenyl-5-chlorobenzimidazole (XI) [4], other conditions being unchanged, rose to 72% of the theoretical, and then, upon further increase in the concentration of the hydrochloric acid, fell to 51% (in 35% hydrochloric acid).



Thus, in this case too, the theoretical consequences that resulted from the reaction mechanism we had elaborated were fully confirmed. The less basic amine, having a lower electron-donor tendency, reacted with greater difficulty with carboxylic acids, but its salts were more easily hydrolyzed with water. Therefore, while in hydrochloric acid of the optimal concentration the yield of benzimidazole derivative from 3,4-diaminobenzene was considerably lower than from o-phenylenediamine, in 35% hydrochloric acid the former condensed even somewhat better than the latter.

From all that has been said, it follows that the o-diamines of the benzene series, both the more and the less basic than o-phenylenediamine, condense with carboxylic acids in aqueous hydrochloric acid medium under pressure, with much more difficulty than o-phenylenediamine does. None the less, this method is completely applicable for the preparation of benzimidazole derivatives, with the exception of those cases where the great tendency to oxidation of the o-diamine is an obstacle to the course of the condensation.

EXPERIMENTAL

I. 2-(β -Phenylethyl)-benzimidazole

3 g of phenylpropionic acid* and 2.1 g of o-phenylenediamine were heated in a sealed tube with 10 ml of 20% hydrochloric acid for 1 hour. The reaction mass was treated with ammonia, and the base which separated out was crystallized several times from benzene containing naphtha. Platelets with m.p. 189-190° were obtained. Yield 4.2 g (97% of the theoretical).

0.1652 g substance: 18 ml N₂ (18°, 768 mm).

Found %: N 12.9.

C₁₅H₁₄N₂. Calculated %: N 12.6.

The hydrochloride of 2-(β -phenylethyl)-benzimidazole was obtained by dissolving the base in hot 5% hydrochloric acid. It crystallized out upon cooling.

It was in the form of needles with m.p. 268-270°. It was very soluble in hot water, and was salted out upon the addition of hydrochloric acid.

II. Benzimidazole Derivatives from 3,4-Toluylenediamine

3,4-Toluylenediamine was prepared by the reduction of 3-nitro-4-toluidine with sodium sulfide [5] and crystallization of the reaction product from benzene.

2-Phenyl-5-methylbenzimidazole. The Influence of the Concentration of Hydrochloric Acid on the Yield of Product. A mixture of 0.01 mole of 3,4-toluylenediamine and 0.01 mole of benzoic acid was heated for 40 minutes at 180-185° in 10 ml of hydrochloric acid of different concentrations. The yield of product varied with the concentration of hydrochloric acid as follows:

Concentration of hydrochloric acid (%)	Yield of 2-phenyl-5-methyl benzimidazole (% of theory)
10	48
15	50
20	53
25	51
35	3

Directions for Preparation. 6.1 g of 3,4-toluylenediamine and 6.1 g of benzoic acid were heated in a sealed tube with 30 ml of 20% hydrochloric acid, 1 hour

* Phenylpropionic acid was prepared by the hydrogenation of cinnamic acid with hydrogen and nickel according to Regnault's method, in alcoholic solution. The reaction goes easily and quickly.

at 190-200°. The reaction product was filtered off from the intensely blue mother liquor and crystallized several times from dilute hydrochloric acid; during the first crystallization, several drops of a solution of chromic acid were added to the solution to destroy the dye. In the other crystallizations, activated carbon was used.

The long white needles of the hydrochloride melted at 274-275°. Yield 8 to 8.5 g. The free base was obtained by treatment of the salt with ammonia, followed by crystallization from aqueous alcohol. M.p. of the base, 241-242°.

2-Benzyl-5-methylbenzimidazole. 3.66 g of 3,4-toluylenediamine and 4.08 g of phenylacetic acid were heated in a sealed tube for 1 hour at 190° with 25 ml of 10% hydrochloric acid. A dark, liquid, tarry mass was obtained. This was separated from the mother liquor, dissolved in hot water, and treated with activated carbon. Concentrated hydrochloric acid was then added to the cooled solution. Needles of the salt of the benzimidazole derivative separated out. After repeated purification, white needles with m.p. 61-63° were obtained. Yield 4.5 g.

The free base was prepared by treating a solution of the salt with ammonia. It precipitated in the form of a tar which soon, however, solidified.

The base crystallized from aqueous alcohol in needles with m.p. 150-151°.

0.0607 g substance: 6.9 ml N₂ (18°, 758 mm).

Found %: N 13.3.

$C_{14}H_{14}N_2$. Calculated %: N 13.32.

2-(β-Phenylethyl)-5-methylbenzimidazole. 5.6 g of toluylenediamine and 7.5 g of phenylpropionic acid were heated in a sealed tube with 40 ml of 15% hydrochloric acid for 1 hour at 180°. The dark liquid, tarry mass obtained was separated from the mother liquor, and dissolved in hot water. Concentrated hydrochloric acid was added to the cold solution, and the product crystallized out. After several crystallizations, the melting point was 82-83.5°. Yield 6.8 g.

The free base was obtained by treatment of a solution of the salt with ammonia. It precipitated out in the form of a tar, which soon solidified.

After several crystallizations from alcohol containing water, needles were obtained with m.p. 134-136°.

0.1421 g substance: 15 ml N₂ (18°, 768 mm).

Found %: N 12.53.

$C_{15}H_{16}N_2$. Calculated %: N 12.50.

III. Benzimidazole Derivatives from 3,4-Diaminophenetole

3,4-Diaminophenetole was prepared by the catalytic reduction of 3,4-dinitrophenetidine by hydrogen in the presence of nickel, according to Regnault's method, in alcoholic medium. After removal of the catalyst and distillation of the alcohol in a stream of carbon dioxide, the product was crystallized from naphtha.

From 12 g of the nitro compound there was obtained 7.5 g of crystalline 3,4-diaminophenetole, with m.p. 79-81°.

2-Phenyl-5-ethoxybenzimidazole. 1.5 g of 3,4-diaminophenetole and 1.22 g of benzoic acid were heated in a sealed tube from which the air had been exhausted, for 4 hours at 170-180°. The sticky, non-solidifying tar which was obtained was crystallized several times from dilute hydrochloric acid. The white needles of the salt of the benzimidazole derivative melted at 249-250°. Yield 1.3 g.

0.0940 g substance: 8.2 ml N_2 (18°, 760 mm).

0.1502 g substance: 5.5 ml 0.1 N $AgNO_3$.

Found %: N 10.23; Cl 12.99.

$C_{15}H_{14}ON_2 \cdot HCl$. Calculated %: N 10.22; Cl 12.93.

The free base was obtained by treating the solution of the salt with ammonia. It was obtained in the form of a tar which solidified only very slowly, to give a solid with m.p. 51-53°. Crystallization from aqueous alcohol and other solvents did not raise this melting point.

2-Benzyl-5-ethoxybenzimidazole. 1.5 g of 3,4-diaminophenetole and 1.4 g of phenylacetic acid were heated in a sealed tube from which the air had been exhausted, for 4 hours at 170-180°. The non-solidifying tarry mass obtained was crystallized from dilute hydrochloric acid. Long white needles of the salt of the benzimidazole derivative were obtained, with m.p. 189°. Yield 1.3 g.

The free base was obtained by treating an aqueous solution of the salt with ammonia, and then crystallizing from aqueous alcohol. It was in the form of needles with m.p. 162-163°.

0.0717 g substance: 6.9 ml N_2 (19°, 768 mm).

Found %: N 11.3.

$C_{16}H_{16}ON_2$. Calculated %: N 11.11.

2-(β -Phenylethyl)-5-ethoxybenzimidazole. 3.5 g of 3,4-diaminophenetole and 4 g of phenylpropionic acid were heated in a sealed tube from which the air had been exhausted for 4 hours at 170-180°. The tarry mass obtained was crystallized from dilute hydrochloric acid. White needles were obtained with m.p. 216-217°. Yield 5 g.

The base, obtained by treatment of the salt with ammonia, crystallized from aqueous alcohol in platelets with m.p. 151-152°.

0.1125 g substance: 0.3165 g CO_2 ; 0.0701 g H_2O .

0.0621 g substance: 5.6 ml N_2 (18°, 758 mm).

Found %: C 76.72; H 6.93; N 10.57.

$C_{17}H_{18}ON_2$. Calculated %: C 76.68; H 6.76; N 10.52.

IV. Benzimidazole Derivatives from 3,4-Diaminoanisole

3,4-Diaminoanisole was prepared by the catalytic reduction of 3,4-nitroanisidine with nickel, according to Regnault's method, in alcoholic medium. After removal of the catalyst and distillation of the alcohol in a current of carbon dioxide, the dark non-solidifying liquid that remained was distilled twice in vacuum. The boiling point was 140-141° at 5 mm residual pressure. A faintly yellowish, very viscous liquid was obtained, which soon solidified to give a white product with m.p. 50-52°. The product very quickly darkened upon standing in air, and even in a sealed ampoule.

2-Phenyl-5-methoxybenzimidazole. 1.4 g of 3,4-diaminoanisole and 1.22 g of benzoic acid were heated in a tube from which the air had been exhausted for 4 hours at 170-180°. The tar obtained was crystallized several times from dilute hydrochloric acid. Needles were obtained with m.p. 255-237°. Yield of salt, 0.8 g.

0.0736 g substance: 6.9 ml N_2 (18°, 760 mm).

0.1550 g substance: 5.7 ml 0.1 N $AgNO_3$.

Found %: N 10.98; Cl 13.47.

$C_{14}H_{12}ON_2 \cdot HCl$. Calculated %: N 10.77; Cl 13.63.

The free base was obtained by treating the salt with ammonia. It was in the form of a tar which soon solidified. After recrystallization from aqueous

alcohol, the m.p. was 142°.

2-Benzyl-5-methoxybenzimidazole. 2.8 g of 3,4-diaminoanisole and 2.72 g of phenylacetic acid were melted together for 4 hours at 170-180° in a sealed tube from which the air had been exhausted. The tar obtained was crystallized from dilute hydrochloric acid. White needles were obtained with m.p. 176-178°. Yield 3.6 g.

0.0990 g substance: 8.7 ml N₂ (18°, 764 mm).

0.1357 g substance: 4.9 ml 0.1 N AgNO₃.

Found %: N 10.38; Cl 12.81.

C₁₅H₁₄ON₂·HCl. Calculated %: N 10.22; Cl 12.93.

The free base was obtained in the form of an easily liquefied tar, which hardened, and then melted at 46°.

2-(β-Phenylethyl)-5-methoxybenzimidazole. 2.8 g of the diamine and 3 g of phenylpropionic acid were melted for 4 hours at 170-180° in a tube from which the air had been exhausted. The tar obtained was crystallized from dilute hydrochloric acid. White needles were obtained with m.p. 239-241°. Yield 3.5 g.

0.0942 g substance: 7.9 ml N₂ (18°, 760 mm).

0.1703 g substance: 5.9 ml 0.1 N AgNO₃.

Found %: N 9.83; Cl 12.3.

C₁₆H₁₆ON₂·HCl. Calculated %: N 9.72; Cl 12.33.

The free base was obtained by treatment of the salt with ammonia. After crystallization from alcohol, it melted at 128-130°.

V. Benzimidazole Derivatives from 3,4-Diaminobenzene

3,4-Diaminobenzene was prepared by the reduction of 3-nitro-4-aminobenzene with sodium sulfide and crystallization of the reaction product from benzene containing naphtha.

2-Phenyl-5-chlorobenzimidazole. (Influence of the Concentration of Hydrochloric Acid upon the Yield of Product). A mixture of 0.01 mole of 3,4-diaminobenzene and 0.01 mole of benzoic acid was heated for 40 minutes at 180-185° in 10 ml of hydrochloric acid of different concentrations. The variation of the yield of product with the concentration of the hydrochloric acid was as follows:

Concentration of hydrochloric acid (%)...	5	10	15	20	25	35
Yield of 2-phenyl-5-chlorobenzimidazole (in % of theory).....	28	42	49.5	58	72	51

Properties of the Product. The free base crystallized from aqueous alcohol in the form of small white leaves. M.p. 210°. The hydrochloride had very little solubility in water. It melted at 290-291°.

SUMMARY

1. o-Diamines of the benzene series, both those that are more basic and those that are less basic than o-phenylenediamine, condense with much more difficulty than the latter with carboxylic acids in aqueous hydrochloric acid medium of optimal concentration under pressure. None the less, this method is completely applicable to the preparation of benzimidazole derivatives, with the exception of those cases where the great tendency of the o-diamine to oxidation is an obstacle to the course of the condensation.

In the latter case, benzimidazole derivatives can be obtained successfully by fusing the components at 180° in the absence of the oxygen of the air.

2. Using the condensations of 3,4-toluylenediamine and 3,4-diaminochlorobenzene with benzoic acid as examples, the conclusions we had drawn earlier [1] about the mechanism of the formation of benzimidazole derivatives in acid medium and the influence of the basicity of the original amine on the course of this reaction were confirmed.

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March 27, 1948.

2-ARYLAMINOPROPIONITRILES

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The reaction for the addition of aliphatic and heterocyclic amines to acrylonitrile has received a certain amount of investigation both in Russian [1] as well as in the foreign [2] literature. The amines usually studied add easily to acrylonitrile simply in the cold or upon heating, although in some cases they require the presence of catalysts. As catalysts, metals (copper, nickel) or their salts, as well as metal oxides, hydrated oxides, and alcoholates [3] have been used. In several cases, basic organic catalysts, like "Triton B" [4] (an aqueous solution of benzyltrimethylammonium hydroxide) have been utilized.

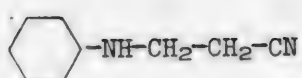
However, the use of these catalysts in the addition of aromatic amines to acrylonitrile does not give positive results. Up to the present, no suitable method has been found for the preparation of 2-arylamino-*propionitriles*. We need only note the following attempts undertaken for this purpose. A German patent [5] refers to the use as a catalyst in this reaction of a concentrated sulfuric acid, while the reaction mixture is heated in a sealed tube at 180°. F. Whitmore and coauthors [6] report that all attempts to add anisidine to acrylonitrile were unsuccessful. E. Elderfield and his coworkers [7] described the condensation product of *p*-anisidine and acrylonitrile obtained in the presence of acetic acid used as catalyst, but this product did not give satisfactory figures upon analysis, and had too high a boiling point. In the opinion of the authors, this was due to the presence of stable contaminating substances.

We were able to observe that 2-arylamino-*propionitriles* could be obtained in good yield by heating salts of aryl amines (acetates, hydrochlorides, phosphates) with acrylonitrile. In this way, we obtained 2-arylamino-*propionitriles*, in some cases in almost quantitative yield (98%), especially when we heated the aromatic amine with acrylonitrile in the presence of the aryl amine salts indicated above as catalysts.

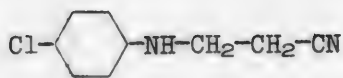
The use of the acetates of the aromatic amines appeared to be most convenient, as these salts are unstable, and decompose upon heating. This permitted us immediately after heating to obtain the product in pure form by distillation in vacuum.

If phosphates and hydrochlorides are used, a solvent is required in order to obtain a homogeneous mass. After heating, the reaction mixture is treated with alkali and extracted with benzene. The yields of arylamino-*propionitriles* with phosphates and hydrochlorides is less than when the acetates are used.

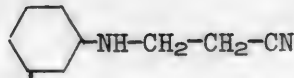
2-Arylamino-*propionitriles* are thick oils, which distill in vacuum without decomposition. Upon cooling, they solidify, and can then be obtained in crystalline form. With hydrochloric acid, they give unstable salts which are partially decomposed by water. We obtained the following 2-arylamino-*propionitriles*:



(2-phenylaminopropionitrile)

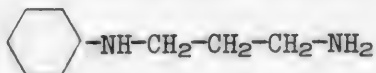


2-(p-chlorophenyl)-aminopropionitrile

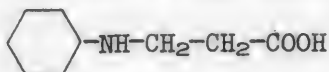


2-(m-chlorophenyl)-aminopropionitrile

To confirm the structure of the 2-arylaminopropionitriles obtained, their simplest representative, 2-phenylaminopropionitrile, was reduced to 3-phenylaminopropylamine [8].



The resulting diamine was analyzed as the free base, the hydrochloride, and the picrate. In addition, 2-phenylaminopropionitrile was heated with hydrochloric acid, and hydrolyzed to give 2-phenylaminopropionic acid:



which in its properties and melting point was identical with the same acid obtained in another manner (C. Bischoff and Nitz [9]).

After the beginning of the present work, the work of A. Terentyev, A. Kost, and V. Potanov, [10] appeared, on the addition of N-ethylamine to acrylonitrile.

The conditions of reaction described in their work, as well as in a number of patents cited, is essentially different from the method we have described here.

The authors of the present work express their acknowledgement to K.S. Topchiev for his valuable advice in the course of this work.

EXPERIMENTAL

2-Phenylaminopropionitrile. a) With aniline acetate. 46.5 g of aniline (0.5 mole), 27.5 g of acrylonitrile (0.52 mole) and 30 g of aniline acetate (0.19 mole) were heated in a flask with a reflux condenser on an oil bath at 120-140° for 14 hours. The reaction mixture was distilled in vacuum, the 2-phenylaminopropionitrile distilling over at 160° (6 mm) in the form of a colorless oil, which solidified after cooling. The yield was 74.3 g, or 98% of theory, basing the calculation on the acrylonitrile. The product was crystallized from aqueous alcohol. It melted at 49°.

4.529 mg substance: 0.764 ml N₂ (26°, 750 mm).

4.0270 mg substance: 0.677 ml N₂ (25°, 749 mm).

Found %: N 19.00, 18.97.

C₉H₁₀N₂. Calculated %: N 19.17.

2-Phenylaminopropionitrile Hydrochloride. To an absolute alcohol solution of 2-phenylaminopropionitrile, alcoholic hydrochloric acid was added until there was an acid reaction to Congo Red. The hydrochloride obtained was precipitated with ether. It was in the form of white prisms which melted at 128°. Upon solution in water, it partially hydrolyzed. It was soluble in alcohol, insoluble in ether.

0.2016 g substance: 10.94 ml 0.1 N NaOH.

0.2000 g substance: 10.94 ml 0.1 N NaOH.

Found %: Cl 19.25, 19.40.

C₉H₁₀N₂·HCl. Calculated %: Cl 19.42.

b) With Aniline Hydrochloride. 23.3 g of aniline (0.25 mole), 13.5 g of

acrylonitrile (0.25 mole), and 10 g of aniline hydrochloride (0.08 mole), and 30 ml of diluted alcohol were heated in a flask with a reflux condenser on an oil bath for 6 hours. After the reaction mixture had been treated with a solution of alkali, the oil which separated out was extracted with benzene. After the benzene had been distilled off, the residue was distilled in vacuum. 21 g of aniline was recovered. The 2-phenylaminopropionitrile distilled over at 171° (10 mm), and melted at 49°. The yield was 8.8 g, or 60% of the theoretical, calculated on the basis of the aniline which had reacted.

c) With Aniline Phosphate. 20.5 g of aniline (0.22 mole), 14 g of acrylonitrile (0.25 mole), 3.9 g of aniline phosphate (0.01 mole), and 60 ml of diluted alcohol were heated in a flask with a reflux condenser on an oil bath at 120-140° for 14 hours. The reaction mixture was treated with a solution of alkali, and the oil which separated out was extracted with benzene. After the benzene had been driven off, the residue was distilled in vacuum. The aniline recovered amounted to 10.5 g; 10.4 g of 2-phenylaminopropionitrile was obtained, or 64% of the theoretical, calculated on the basis of the aniline which had reacted. The b.p. was 150° at 3 mm, the m.p. 49°.

3-Phenylaminopropylamine-1. 2-Phenylaminopropionitrile (30 g) was reduced in isoamyl alcohol (500 ml) with metallic sodium (37 g). The diamine obtained was extracted from the solution of amyl alcohol with hydrochloric acid, and the acid solution was concentrated, and made alkaline with a 40% solution of alkali. The product was extracted with benzene and dried over potassium carbonate. After the potash had been removed and the benzene driven off, the 3-phenylaminopropylamine was distilled in vacuum. It boiled at 126-129° (3 mm). The 3-phenylaminopropylamine was a viscous oil with a characteristic amine odor, soluble in water, in mineral acids, and in most organic solvents.

7.217 mg substance: 1.147 ml N₂ (19°, 750 mm).

4.438 mg substance: 0.706 ml N₂ (20°, 745 mm).

Found %: N 18.33, 18.16.

C₉H₁₄N₂. Calculated %: N 18.66.

3-Phenylaminopropylamine Dihydrochloride. Upon the addition of alcoholic hydrochloric acid to an absolute alcohol solution of 3-phenylaminopropylamine, the dihydrochloride precipitated. It was crystallized from alcohol as white tetragonal platelets with m.p. 236°. It was very soluble in water, and in hot alcohol. It did not dissolve in ether.

7.882 mg substance: 0.863 ml N₂ (19°, 763 mm).

6.167 mg substance: 0.696 ml N₂ (19°, 743 mm).

0.2197 g substance: 0.2828 g AgCl.

Found %: N 12.85, 12.90; Cl 31.84.

C₉H₁₄N₂·2HCl. Calculated %: N 12.55; Cl 31.79.

3-Phenylaminopropylamine Picrate. The picrate precipitated out when concentrated aqueous solutions of the base were mixed with picric acid. It crystallized from water in red platelets, with m.p. 125°.

7.314 mg substance: 1.225 ml N₂ (19°, 743 mm).

7.743 mg substance: 1.274 ml N₂ (19°, 748 mm).

Found %: N 19.14, 18.95.

C₉H₁₄N₂·C₆H₂(NO₂)₃OH. Calculated %: N 18.47.

2-Phenylaminopropionic Acid. 2-Phenylaminopropionitrile (14.6 g) was heated with concentrated hydrochloric acid (150 ml) for 5 hours. The hydrochloric acid was distilled off in vacuum on the water bath. The residue was dissolved in a small amount of water and neutralized with ammonia. The oil which separated out was extracted with ether, and the ether solution dried over potash. After removal of the potash, the ether was distilled off, and the oil which remained was

allowed to stand in a vacuum-dessicator. After several days, the oil crystallized. The yield was 12 g. It was crystallized from a mixture of chloroform and petroleum ether in platelets that melted at 58-59°. (C. Bischoff gives the m.p. as 59-60°). The 2-phenylaminopropionic acid dissolved in water, acids, alkalies, and in most organic solvents.

2-(p-Chlorophenyl)-aminopropionitrile. 25.5 g of p-chloroaniline (0.20 mole) 13.5 g of acrylonitrile (0.25 mole, and 9.1 g of p-chloroaniline acetate (0.05 mole) were heated on an oil bath at 130-140° for 14 hours. The product of reaction was distilled in vacuum. 12 g of unreacted p-chloroaniline was recovered. The 2-(p-chlorophenyl)-aminopropionitrile distilled over at 182-185° (4 mm). The yield was 20 g, or 72% of the theoretical, calculated on the basis of the p-chloroaniline which had reacted. The oil obtained solidified upon cooling. It crystallized from dilute alcohol in platelets, m.p. 72-73°. The product dissolved in mineral acids, and in alcohol and benzene. It was insoluble in water.

6.762 mg substance: 0.960 ml N₂ (21°, 737 mm).

8.407 mg substance: 1.137 ml N₂ (20°, 751 mm).

0.0938 g substance: 0.0954 g AgNO₃.

0.1006 g substance: 0.0981 g AgNO₃.

Found %: N 15.98, 15.57; Cl 20.15, 20.35.

C₉H₉N₂Cl. Calculated %: N 15.53; Cl 19.64.

2-(p-Chlorophenyl)-aminopropionitrile Hydrochloride. Alcoholic hydrochloric acid was added to an alcoholic solution of the nitrile until Congo Red changed color. The hydrochloride obtained was precipitated with ether, in the form of white prisms with m.p. 134-136°. It partially hydrolyzed on dissolving in water. It was soluble in alcohol, insoluble in ether.

0.1292 g substance: 5.967 ml 0.1 N NaOH.

Found %: Cl (ionic) 16.37.

C₉H₉N₂Cl·HCl. Calculated %: Cl (ionic) 16.33.

2-(m-Chlorophenyl)-aminopropionitrile. 50 g of m-chloroaniline acetate (0.26 mole), and 14 g of acrylonitrile (0.26 mole) were heated on an oil bath at 120-140° for 14 hours. The reaction product was distilled in vacuum. 10.8 g of unreacted m-chloroaniline was recovered. The 2-(m-chlorophenyl)-aminopropionitrile distilled over at 187-189° (9 mm) in the form of a colorless oil. It solidified upon cooling. The yield was 26.8 g, or 55% of the theoretical, calculated on the basis of m-chloroaniline used, and 81% on the basis of the m-chloroaniline which had reacted. The product crystallized from aqueous alcohol in the form of white platelets with m.p. 48°. It dissolved in dilute mineral acids, alcohol, and benzene. It did not dissolve in water.

7.436 mg substance: 1.010 ml N₂ (21°, 749 mm).

7.024 mg substance: 0.941 ml N₂ (21°, 749 mm).

0.1016 g substance: 0.0951 g AgNO₃.

0.1005 g substance: 0.0967 g AgNO₃.

Found %: N 15.54, 15.33; Cl 19.53, 20.09.

C₉H₉N₂Cl. Calculated %: N 15.53; Cl 19.64.

2-(m-Chlorophenyl)-aminopropionitrile Hydrochloride. Alcoholic hydrogen chloride was added to an alcoholic solution of chlorophenylaminopropionitrile until Congo Red changed color. The hydrochloride formed was precipitated with ether in the form of white prisms, m.p. 125-126°. The product dissolved in alcohol and in water (in which it is partially hydrolyzed). It did not dissolve in ether.

0.2130 g substance: 9.743 ml 0.1 N NaOH.
0.1336 g substance: 6.141 ml 0.1 N NaOH.
Found %: Cl (ionic) 16.22, 16.30.
 $C_9H_9N_2Cl \cdot HCl$. Calculated %: Cl (ionic) 16.33.

SUMMARY

1. A new method has been described for the preparation of 2-arylamino-
propionitriles by heating the salts of aryl amines with acrylonitrile. 2-Phenyl-
aminopropionitrile, 2-(p-chlorophenyl)-aminopropionitrile, and 2-(m-chlorophenyl)-
aminopropionitrile have been obtained.

2. The structure of the nitriles obtained has been confirmed for 2-phenyl-
aminopropionitrile, by reduction to 3-phenylaminopropylamine-1 and by hydrolysis
to 2-phenylaminopropionic acid.

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THE CLEAVAGE OF LIGNIN WITH METALLIC SODIUM IN LIQUID AMMONIA. III

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In previous communications we have mentioned the fact that metallic Na in a solution of liquid NH_3 almost completely decomposes cuprammonium lignin, as well as other forms of lignin, to give low-molecular weight substances. We thus obtained monomeric substances which were extracted by means of ether from aqueous alkaline solution, as well as monomeric acids, carbohydrates, and substances of an acid character with molecular weight in the neighborhood of 2000 (cf. Communications I and II). This communication will describe the investigation of the compounds extracted from alkaline solution by means of ether.

At the end of the reaction of the cuprammonium lignin with metallic sodium, the ammonia was driven off, and the small amount left was removed with dry nitrogen which had been freed of oxygen. The product of reaction that remained was covered with moist ether. After a day or two, the ether was poured off, the solid residue was dissolved in water (it dissolved completely) and the alkaline solution was extracted five times with ether. The ether extracts, which had a slight yellowish color, were united, dried over sodium sulfate, and the ether distilled off. There remained in the flask a yellow syrupy substance with a characteristic odor that was somewhat reminiscent of the odor of eugenol. The yield of the first treatment of 15 g of lignin with metallic Na (11.25 g) amounted on an average to 0.4 g, or 2.6%. From a total of 93 g of cuprammonium lignin whose treatment was repeated 9 times, there was obtained 7.84 g, or 8.43%.

The substance was in the form of a yellowish syrup with an admixture of solid white particles. When this mixture was treated with alcohol, the syrupy substance dissolved completely, but the white, solid paraffin-like particles remained undissolved. The solid residue was washed with alcohol several times more. After the alcohol was distilled off, the syrup was no longer contaminated with a solid substance.

The yield of syrupy substance (I) from 93 g of lignin was 8.01%. The yield of paraffin-like substance (II) from 93 g of lignin was 0.39 g, or 0.4%.

The syrupy product distilled in vacuum without decomposition. After distillation it was an almost colorless oil with a fairly pleasant odor resembling the odor of eugenol. It had the following properties:

B.p. 108° (2 mm), $112-114^\circ$ (3 mm), $123-125^\circ$ (10 mm), d_4^{20} 1.0209; n_D^{20} 1.5212.

Molecular weight, by Rast's method, 168 (average of 2 determinations)

Found %: C 72.12; H 8.84.

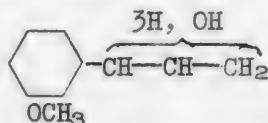
$\text{C}_{10}\text{H}_{14}\text{O}_2$. Calculated %: C 72.24; H 8.43.

Thus, the substance had the formula $\text{C}_{10}\text{H}_{14}\text{O}_2$ (molecular weight 166). It contained one OH group (OH content, by Tserevitinov's method, 10.32%; calculated

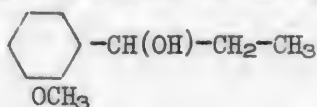
for $C_{10}H_{14}O_2$, 10.24%).

The substance contained a methoxyl group. However, during the determination of Tseizelya's method, we always obtained figures somewhat lower than the theoretical.

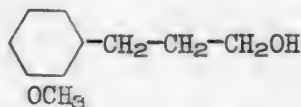
In view of the fact that the substance was extracted by ether from alkaline solution, we assumed that the hydroxyl group was an alcoholic one, and that the product was a *m*-methoxyphenylpropyl alcohol:



as, upon oxidation with permanganate, we obtained *m*-methoxybenzoic acid. However, the yield was very small, and this caused some doubt. Seeing that we had at our disposal only a very small amount of the substance, we synthesized for purposes of comparison with it the alcohols



and

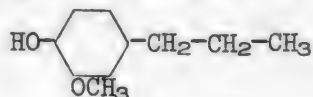


These compounds are known. One was obtained by Easson and Stedman [1], the other by Robinson and Schlittler [2].

The properties of these alcohols, however, were different from that of the substance under investigation. Under the conditions we used, they did not give crystalline derivatives - benzoates and urethanes.

A closer chemical investigation of the substance which we had separated from lignin showed that it was soluble in a dilute solution of caustic soda and gave a white solid salt with a concentrated solution with caustic soda. The white salt dissolved upon the addition of water.

Thus, the substance was a phenol, despite the fact that it could be extracted by means of ether from a comparatively concentrated (5%) solution of NaOH. With benzoyl chloride, it gave, by the Schotten Bauman method, a crystalline benzoate, melting at 74-75°. Upon heating with phenyl isocyanate in toluene, a crystalline phenylurethane was formed, with m.p. 122°. This forced us to assume that the substance under investigation was dihydroeugenol:



For dihydroeugenol, it is known that:

d_{18}^{15} 1.0440; b.p. 128-130° (13 mm); phenylurethane, m.p. 117.5-118° [3]; benzoate, m.p. 73° [4].

Recently, Gauthier [5] obtained dihydroeugenol by the catalytic hydrogenation of eugenol with Regnault's nickel at room temperature. Gauthier gives the following constants for it:

B.p. 126° (14 mm); phenylurethane, m.p. 122°; $n_D^{17.5}$ 1.5220; d_4^{18} 1.0398; benzoate, m.p. 74-75°.

The melting points of the derivatives of the substance under investigation agree precisely with those given by Gauthier for dihydroeugenol.

To complete the identification, we prepared dihydroeugenol from eugenol by hydrogenation, following Gauthier's method, and obtained a compound whose

properties agreed accurately with Gauthier's preparation.

B.p. 246° ; $n_D^{17.5}$ 1.5220; benzoate, m.p. $74-75^{\circ}$; phenylurethane, m.p. 122° .

A mixed test of the benzoates of the compound from lignin and of dihydroeugenol gave m.p. $74-75^{\circ}$, i.e., no depression. A mixed test of the phenylurethanes of the substance under investigation and of dihydroeugenol also gave no depression; m.p. 122° .

Thus, the formation of dihydroeugenol by the decomposition of lignin with metallic sodium in liquid ammonia has been completely confirmed.

The formation of a small amount of m-methoxybenzoic acid during the oxidation with permanganate was apparently due to the admixture of m-methoxyphenylpropyl alcohol with the dihydroeugenol, as both had the same composition.

It became clear to us that dihydroeugenol was formed in this case as a result of the reduction of fragments of the lignin molecule of the type of phenylpropane derivatives, obtained as a result of the breaking of ether bonds according to Shorygin's reaction.

To confirm this hypothesis, we subjected coniferyl alcohol to treatment with metallic sodium in a solution of liquid NH_3 under the conditions we had used for lignin.

We obtained coniferyl alcohol by the emulsin cleavage of coniferin extracted from the cambial sap of the pine. It had m.p. 74° ; this corresponded to the data of Tiemann and Haarmann [6].

3 g of coniferyl alcohol was dissolved in 400 ml of liquid NH_3 and 3 g of metallic Na was added, based on a calculation of 4 atoms of Na per molecule, plus 100% excess. The reaction was allowed to continue for 5 days while the reaction mixture was cooled with dry ice. At the end of this period, the Na had almost completely reacted. The ammonia was driven off, and the product of reaction that remained in the vessel was covered with moist ether. The ether was decanted into a separatory funnel, and the residue in the reaction vessel was dissolved in water, in which it was completely soluble. The alkaline solution was extracted with ether five times, then acidified and again extracted with ether.

After the ether had been distilled off from the ether extract of the alkaline solution, 1.5 g (1) of an oily liquid was obtained. From the ether extract of the acid liquid, 0.9 g (2) was obtained. Total yield amounted to 2.5 g.

As far as external characteristics went, both substances were very similar (although product (2) had a somewhat darker color).

Substance (1) boiled at 103° (2 mm) and with a concentrated solution of caustic soda gave a solid white salt, soluble in water.

Found %: C 72.42; H 8.54.

$C_{10}H_{14}O_2$. Calculated %: C 72.2; H 8.43.

The benzoate, obtained by the Schotten Bauman reaction, melted at $74-75^{\circ}$. Its carbon and hydrogen content corresponded to the formula $C_{17}H_{18}O_3$. Its phenyl urethane melted at 122° , and contained an amount of nitrogen corresponding to the formula.

Substance (2) boiled at about the same temperature. Part of it, however, became tarry during the distillation, and remained in the distillation flask in the form of a dark tarry mass. Substance (2) gave the same benzoate, with m.p. $74-75^{\circ}$, and the same urethane, with m.p. 122° . Mixed tests of the derivatives of substances (1) and (2) gave no depression. It is obvious that the two substances, (1) and (2), extracted by ether from the alkaline and the acid solutions, were identical.

Mixed tests of the benzoates and urethanes of substances (1) and (2) with the benzoate and urethane of dihydroeugenol also gave no depression. Therefore, the action of a solution of metallic Na in liquid NH_3 on coniferyl alcohol gives dihydroeugenol in a yield of 86%.

It is of interest to note that dihydroeugenol can be extracted to a considerable extent by ether from a solution in 5% aqueous alkali. It is obvious that the hydrocarbon chain greatly decreases the acid properties of the phenolic OH groups. In a special experiment with pure dihydroeugenol, we succeeded, by five extractions with ether from a solution in 3% caustic soda and shaking in a separatory funnel, in removing the dihydroeugenol from solution almost completely.

The reduction of unsaturated alcohols by metallic Na in liquid NH_3 had been observed back in 1906 by Chablay [7]. He showed that allyl alcohol was reduced to propylene by metallic Na in liquid NH_3 . Dupont, Dulon, and Desreux [8] found later that linalool and geraniol were reduced under these conditions, forming one and the same unsaturated hydrocarbon β -methylgeraniolene. Chablay expressed the hypothesis that the only aliphatic alcohols which could be easily reduced were those which contained the CH_2 group in the allyl system. According to Chablay's data [8, 10] aromatic unsaturated alcohols were more difficult to reduce to the hydrocarbons.

Thus, cinnamyl alcohol was hydrogenated by Na in liquid NH_3 at the double bond, forming phenylpropyl alcohol. Phenylpropylene was observed in only negligible quantities.

Birch [11] hydrogenated aromatic alcohols with sodium in liquid NH_3 in the presence of alcohols (amyl, ethyl). Under these conditions, both the saturated as well as the unsaturated alcohols were reduced. With unsaturated aromatic alcohols, the velocity of hydrogenation of the double bond and the reduction of the hydroxyl group depended on the substituents at the carbon atom bound to the OH group, on the position of the double bond, and on the presence of substituents in the benzene ring. It is as yet impossible to say which process (hydrogenation of the double bond or reduction of the OH group) takes place more quickly when metallic Na in liquid NH_3 acts on coniferyl alcohol. With an excess of Na, both processes proceed to completion.

There are well-known old data [12] to the effect that the action of Na amalgam on coniferyl alcohol in alkaline solution gives eugenol in low yield.

It is obvious that in this case reduction of the OH group takes place along with a shift in the double bond.

The formation of dihydroeugenol from cuprammonium lignin during its decomposition with metallic Na in liquid NH_3 , in a yield of about 8%, is a new confirmation of the fact that lignin is in considerable part composed of derivatives of 4-hydroxy-3-methoxyphenylpropane. The fact that dihydroeugenol is very easily formed under the conditions of the experiment from coniferyl alcohol forces us to suppose that the primary product of the decomposition of lignin under the action of Na in liquid NH_3 is a compound of the type of coniferyl alcohol, which is hydrogenated to dihydroeugenol by further action. We even earlier expressed the opinion that the formation of lignin from the coniferin of cambial sap probably took place as a result of condensation with the formation of ether bonds. The high yield of phenol (about 13%), very close to coniferyl alcohol, which is formed at the same time as dihydroeugenol during the decomposition of lignin by sodium in liquid NH_3 , also confirms this supposition.

Thus Claisen's old theory of the relation between lignin and the coniferin of the cambial sap has received genuine confirmation.

We must also recall that Phillips [13,14] has obtained dihydroeugenol by the dry distillation of lignin with zinc dust in an atmosphere of hydrogen. His yield was, it is true, very low (less than 0.5%).

We also investigated the solid paraffin-like substance (II) obtained by the extraction with ether of the aqueous alkaline solution. We have mentioned above that this product was separated from the syrupy substance (I the dihydroeugenol) by treatment with alcohol.

The slightly yellowish paraffin-like substance, insoluble in alcohol, was obtained from 93 g of lignin after nine consecutive treatments with sodium in liquid NH_3 to the amount of 0.39 g. After distillation in vacuum, it was in the form of an absolutely white transparent substance, similar to paraffin:

B.p. $140-145^\circ$ (20 mm); m.p. $43-44.5^\circ$; $n_D^{41.5}$ 1.4640; molecular weight (cryoscopic, in benzene) 246.6 and 244.02.

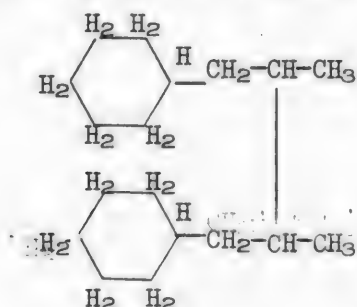
Found %: C 85.36, 85.79; H 14.27, 14.54.

$\text{C}_{18}\text{H}_{34}$. Calculated %: C 86.4; H 13.6; M 250.

The substance was a hydrocarbon with a formula corresponding to $\text{C}_{18}\text{H}_{34}$ or $\text{C}_{18}\text{H}_{36}$. The ratio of carbon to hydrogen corresponded to that for a hydrocarbon of the paraffin or cycloparaffin series.

Considering the probability of hydrogenation of the benzene ring under the conditions present in our reaction (Na in liquid NH_3), we may assume that this hydrocarbon was formed from compounds of the type of phenylpropane (for example, from coniferyl alcohol) themselves formed during the decomposition of the lignin.

In our opinion, the probable formula of the hydrocarbon obtained is:



The possibility of hydrogenation of aromatic compounds (benzene and its derivatives) was recently shown by Wooster and Godfrey [15] as well as by Birch [16]. These investigations showed that the hydrogenation of benzene rings could be easily accomplished by Na in liquid NH_3 in the presence of water or alcohol. Sartoretto and Sova [17] obtained the hydrogenation of benzoic acid during the cleavage by metallic Na in liquid NH_3 of the phenyl ether of 4-carboxyphenol. The role of the alcohol could be played in our case by the hydroxyl groups present in considerable quantity in the original lignin.

Part of these hydroxyl groups belong to the carbon atoms bound to the lignin. That dimerization is possible follows from the work of Schlenk [18], and Shorygin and Skoblinskaya [19].

EXPERIMENTAL

Analysis of the Product of the Cleavage of Lignin Extracted by Ether from the Alkaline Solution

Determination of the molecular weight by Rast's method:

8.6 mg substance; 126.8 mg camphor: Δt 17°.
6.8 mg substance; 123.8 mg camphor: Δt 12.4°.
Found: M 159.09, 176.00.
 d_4^{20} 1.0209.

Analysis

10.73 mg substance: 28.53 mg CO₂; 8.52 mg H₂O.
Found %: C 72.12; H 8.84.
5.36 mg substance: 14.13 mg CO₂; 4.24 mg H₂O.
Found %: C 72.05; H 8.85.
C₁₀H₁₄O₂. Calculated %: C 72.24; H 8.43.
79 mg substance: 10.67 ml CH₄ (0°, 760 mm).
Found %: OH 10.32.
C₁₀H₁₃O(OH). Calculated %: OH 10.24.

Oxidation. 1) 0.35 g of the substance was dissolved in 4 ml of pure acetone. The acetone solution was poured with vigorous stirring into 50 ml of water, forming a fine emulsion. The solution was heated with constant stirring up to 95° for 1.5 hours in order to remove the acetone. The reaction mixture was cooled to 60°, and KMnO₄ was gradually added in 0.1 g portions. A total of 0.7 g was added until a stable rose color was formed. As the permanganate was added, the temperature was gradually raised to 95°. The solution was filtered from the MnO₂ and the excess of KMnO₄ destroyed by the addition of a small amount of Na₂S₂O₃ and H₂SO₄.

The acid was removed from the acid solution by five extractions. The extract was dried over anhydrous Na₂SO₄. After removal of the solvent, the residue which was a yellow syrupy substance, was maintained for a long time in a vacuum dessicator over solid KOH to remove volatile acids. The crystals that remained were recrystallized from water. They were in the form of fine white needles, melting at 104-108°. Yield, 0.05 g.

2) 0.45 g of substance, 0.9 g of KMnO₄. Conditions the same. 0.07 g of acid was obtained, with m.p. 105-106°.

3.63 mg substance: 8.54 mg CO₂; 1.79 mg H₂O.
Found %: C 64.18; H 5.52.
4.36 mg substance: 10.32 mg CO₂; 2.10 mg H₂O.
Found %: C 64.00; H 5.39.
C₈H₈O₃. Calculated %: C 63.15; H 5.30.

Preparation of the Benzoyl Derivative. 0.3 g of the substance was mixed with 15 g of 15% NaOH. The mixture was shaken for 30 minutes with 1.8 g of C₆H₅COCl. The solid substance formed was filtered off, and boiled several times with water in order to remove the excess of C₆H₅COCl and to dissolve the benzoic acid. It was then cooled and filtered. The benzoate was recrystallized twice from alcohol. It was in the form of splendid white shining crystals, melting at 74-75°.

5.073 mg substance: 14.109 mg CO₂; 3.055 mg H₂O.
4.39 mg substance: 12.199 mg CO₂; 2.621 mg H₂O.
Found %: C 75.85, 75.76; H 6.69, 6.64.
C₁₇H₁₈O₃. Calculated %: C 75.53; H 6.71.

The Preparation of the Phenylurethane. 0.3 g of the substance and 0.7 g of phenylisocyanate were boiled in 10 ml of toluene with a reflux condenser for 6 hours. The toluene was distilled off and the residue began to crystallize after rubbing with a glass rod. After two recrystallizations from alcohol, small snow white needles were obtained with m.p. 122°.

The Reaction of Coniferyl Alcohol with a Solution of Metallic Na
in Liquid NH₃

3 g of coniferyl alcohol was dissolved in 400 ml of liquid NH₃ in a reaction vessel. 3 g of metallic Na was then added. As the reaction progressed, the sodium salt of coniferyl alcohol precipitated; it was insoluble in liquid NH₃. The reaction was allowed to continue for 5 days while the reaction flask was cooled with dry ice. After this time, almost all the Na had reacted. After the NH₃ had been driven off, only a small amount of Na remained in places in the form of a thin layer on the upper walls of the vessel. The remaining NH₃ was displaced by a current of dried nitrogen which had been purified of oxygen, and 400 mg of moist ether was poured into the flask. The next day, the ether was removed in a separatory funnel, and the residue dissolved in water. An ether extraction was made of the aqueous alkaline solution. The rest of the aqueous alkaline solution was acidified with sulfuric acid and again extracted with ether. After removal of the solvent, there was obtained from the alkaline solution 1.5 g (1) of the substance and from the acid solution 0.9 g (2). Substance (1) was distilled in vacuum. The b.p. was 103° at 2 mm. The almost colorless oil gave, with 20% NaOH, a solid salt which dissolved in water.

4.060 mg substance: 10.774 mg CO₂; 3.090 mg H₂O.

Found %: C 72.42; H 8.54.

6.530 mg substance: 17.351 mg CO₂; 4.904 mg H₂O.

Found %: C 72.51; H 8.40.

C₁₀H₁₄O₂. Calculated %: C 72.24; H 8.43.

Preparation of the Benzoate. 0.3 g of the substance was shaken in a small sealed flask with 1.8 g of C₆H₅COCl and 15 ml of 15% NaOH. A white solid mass quickly formed. It was boiled with water several times and then recrystallized from alcohol. It was in the form of snow-white crystals with m.p. 74-75°.

5.782 mg substance: 10.49 mg CO₂; 2.270 mg H₂O.

Found %: C 75.70; H 6.71.

3.650 mg substance: 10.151 mg CO₂; 2.195 mg H₂O.

Found %: C 75.90; H 6.73.

C₁₇H₁₈O₃. Calculated %: C 75.53; H 6.71.

Preparation of the Urethane 0.3 g of the substance, 0.6 g of phenyl isocyanate, and 10 ml of toluene were boiled for 6 hours. The toluene was distilled off and the residue recrystallized from alcohol in the form of small white needles, with m.p. 122°.

0.9 g of substance (2), obtained by the extraction from the acid liquid, was distilled in vacuum. B.p. 103° at 2 mm; about 0.3 g remained in the distilling flask in the form of a tarry mass. The benzoate was prepared in the same way, and melted at 74-75°.

4.2 mg substance: 11.671 mg CO₂; 2.477 mg H₂O.

Found %: C 75.82; H 6.61.

4.66 mg substance: 12.922 mg CO₂; 2.780 mg H₂O.

Found %: C 75.66; H 6.67.

C₁₇H₁₈O₃. Calculated %: C 75.53; H 6.71.

The urethane, obtained in the same way, melted at 122°. A mixed test of benzoates from (1) and (2) gave m.p. 74-75°. A mixed test of urethanes from (1) and (2) gave m.p. 122°.

The Hydrogenation of Eugenol

The eugenol with which we started boiled at 250-252°; n_D^{20} 1.5410.

3 g of it was dissolved in 20 ml of C_2H_5OH . The solution was shaken with 1 g of Regnault's nickel in an atmosphere of electrolytic hydrogen in a hydrogenation vessel at a temperature of 25° . In 5 hours, 400 ml of H_2 was used up. The nickel was filtered off and the solution was extracted with ether. The ether extract gave 2.6 g of dihydroeugenol. B.p. $246-248^\circ$; $n_D^{17.5}$ 1.5220.

The benzoate, obtained by the usual method, melted at $74-75^\circ$; the phenylurethane, at 122° .

A mixed test of the benzoates of the compound from lignin and the benzoate of dihydroeugenol gave m.p. $74-75^\circ$.

A mixed test of the benzoates of the hydrogenation products of coniferyl alcohol and the benzoate of dihydroeugenol gave m.p. $74-75^\circ$.

A mixed test of the phenylurethane of the compound from lignin and the dihydroeugenol urethane gave m.p. 122° .

A mixed test of the phenylurethanes of the reduction products of coniferyl alcohol and the urethane of dihydroeugenol gave m.p. 122° .

The Extraction by Ether of the Alkaline Solution of Dihydroeugenol. 1.5 g of dihydroeugenol was dissolved in 100 ml of 3% NaOH solution. The solution was extracted with ether five times. After drying and removal of the solvent by distillation, 1.2 g of dihydroeugenol was obtained. Thus, ether extraction of the alkaline solution removed 80% of the dihydroeugenol.

Analysis of the Hydrocarbon Obtained by the Cleavage of Lignin

by Metallic Na in Liquid NH_3

0.1122 g substance: 12.05 g benzene: Δt 0.185° .

Found: M 244.02.

5.54 mg substance: 17.34 mg CO_2 ; 7.05 mg H_2O .

Found %: C 85.30; H 14.27.

5.42 mg substance: 17.05 mg CO_2 ; 6.98 mg H_2O .

Found %: C 85.79; H 14.54.

$C_{18}H_{34}$. Calculated %: C 86.32; H 13.68.

SUMMARY

1. The decomposition of cuprammonium lignin by metallic sodium in liquid NH_3 gives about 8% of a monomeric compound which is extracted by ether from the aqueous alkaline solution. It has been shown that this compound is dihydroeugenol.

2. The action of metallic Na in liquid NH_3 upon coniferyl alcohol gives dihydroeugenol in about 86% yield.

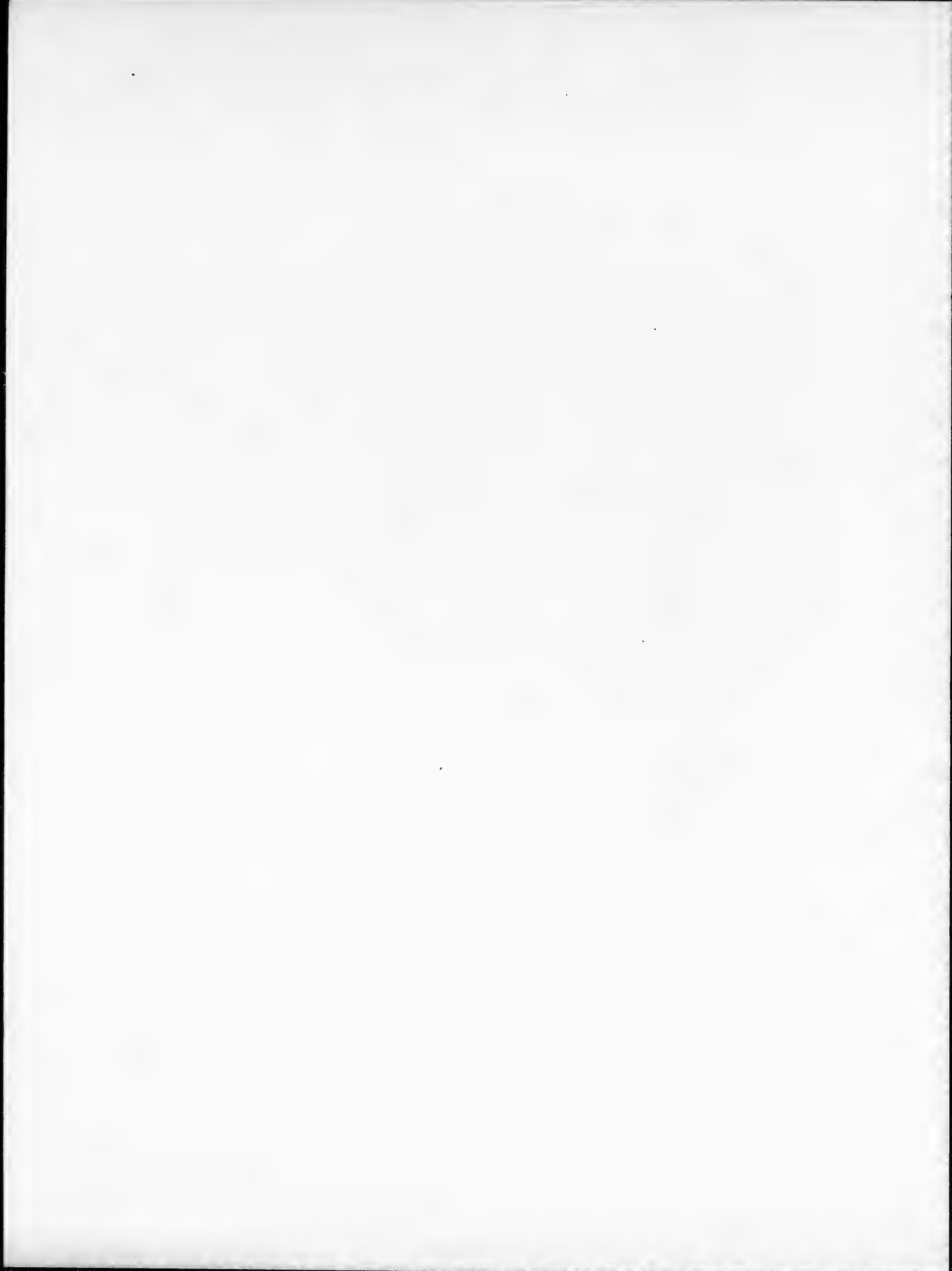
The latter fact forces us to assume that dihydroeugenol is formed from lignin during the reaction with metallic Na in liquid NH_3 by the hydrogenation of the product of decomposition of the lignin, obtained according to Shorygin's reaction.

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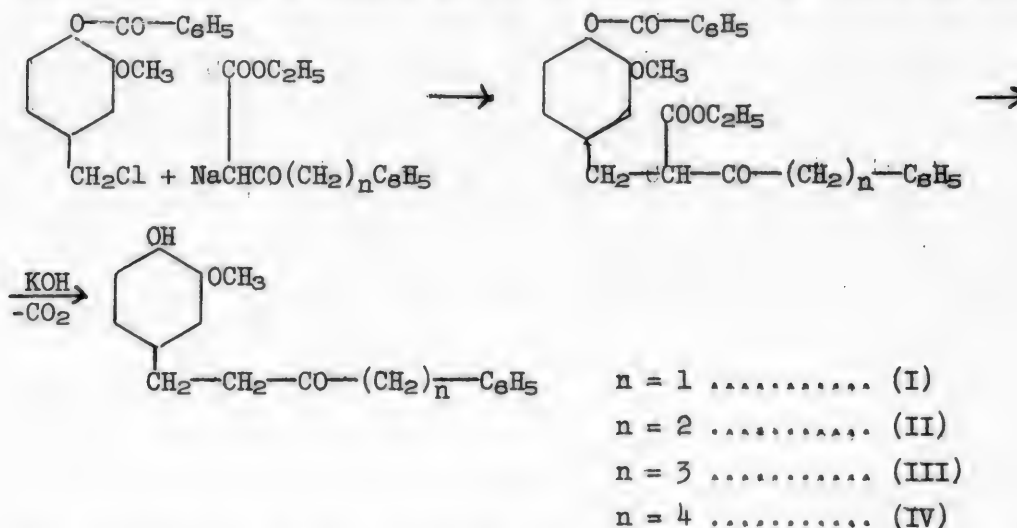
DERIVATIVES OF ZINGERONE IV.

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As has already been shown previously [1], for the synthesis of complicated alkyl-aromatic ketones we can successfully utilize the different γ -substituted derivatives of acetoacetic ester. By this method, we obtained several alkylaromatic derivatives of zingerone.

The course of the synthesis may be represented by the following scheme:



The condensation of the γ -derivatives of acetoacetic ester in the form of their sodium derivatives with benzoylvanillyl chloride [2] was carried out in absolute alcohol-benzene solution with heating. The α -benzoylvanillylacetylacetic acid esters thus obtained are viscous, dark yellow liquids which do not crystallize upon cooling and cannot be distilled in vacuum without decomposition. They are saponified and decarboxylated by treatment with an alcoholic solution of caustic potash. After acidification, the following were isolated: 4-hydroxy-3-methoxyphenylethylbenzyl ketone (I), 4-hydroxy-3-methoxyphenylethyl- β -phenylethyl ketone (II), 4-hydroxy-3-methoxyphenylethyl- γ -phenylpropyl ketone (III), and 4-hydroxy-3-methoxyphenylethyl- δ -phenylbutyl ketone (IV). These compounds were characterized by means of their 2,4-dinitrophenylhydrazines.

An investigation of the synthesized alkyl-aromatic derivatives of zingerone showed that they all had burning taste, like the other substances of this type that we had investigated. 4-Hydroxy-3-methoxyphenylethylbenzyl ketone (I) was almost inactive, but as the number of methylene groups in the residue of the alkyl-aromatic hydrocarbon increased, the burning quality also increased, reaching a value approximately of the same order as with zingerone.

EXPERIMENTAL

4-Hydroxy-3-methoxyphenylethylbenzyl Ketone (I). An alcoholic solution of sodium ethylate, prepared from 0.72 g of metallic sodium in 80 ml of absolute alcohol, was added to a solution of 8 g of γ -benzylacetoacetic ester in 70 ml of absolute alcohol. As the solutions were mixed, the separation of a slightly yellowish voluminous precipitate of the sodium derivative of γ -benzylacetoacetic ester was observed. To the reaction mixture there was added, drop by drop and with vigorous stirring, a solution of 10 g of benzoylvanillyl chloride (m.p. 96-97°) in 200 ml of absolute benzene. After the addition of the chloride, the reaction mixture was heated with a reflux condenser on the water bath for 6 hours, with stirring. Even after 2 hours, the conversion of the voluminous precipitate of sodium benzylacetoacetic ester into the denser precipitate of sodium chloride could be noticed. At the end of the heating, part of the solvent was driven off, and the residue, amounting to 130-150 ml, was poured into 500 ml of water. The oil which separated out was extracted with ether and dried over sodium sulfate. After the removal of the solvent by distillation, the residue, a yellow viscous liquid, was treated with 30 ml of a 30% alcoholic solution of caustic potash, and the solution formed was heated with a reflux condenser on the water bath for 3 hours. After cooling, the reaction product was poured into water. The aqueous solution was extracted with ether, acidified with hydrochloric acid, and boiled together with the oil which separated for one hour, then extracted with ether. After the ether extract had been carefully washed with a bicarbonate solution and water, and dried over sodium sulfate, the ether was distilled off. The residue was distilled twice in vacuum. About 2 g of 4-hydroxy-3-methoxyphenylethylbenzyl ketone was obtained, with b.p. 190-193° at 2 mm. Upon standing, the compound crystallized. It was recrystallized from a mixture of ether with petroleum ether. The m.p. was 48-49°. The product was in the form of rectangular platelets, very soluble in ether, alcohol, benzene, and chloroform, and insoluble in water and petroleum ether.

3.498 mg substance: 9.680 mg CO₂; 2.161 mg H₂O.

Found %: C 75.47; H 6.91.

C₁₇H₁₈O₃. Calculated %: C 75.55; H 6.66.

2,4-Dinitrophenylhydrazone, after being recrystallized twice from alcohol, was in the form of yellow needles, with m.p. 134°.

3.730 mg substance: 0.412 ml N₂ (15°, 746 mm).

Found %: N 12.85.

C₂₃H₂₂O₆N₄. Calculated %: N 12.44.

4-Hydroxy-3-methoxyphenylethyl- β -phenylethyl ketone (II). To a solution of 8 g of γ -benzylacetoacetic ester in 70 ml of absolute alcohol there was added an alcoholic solution of sodium ethylate, prepared from 0.84 g of metallic sodium and 80 ml of absolute alcohol. To the alcoholic solution of sodium benzylacetoacetic ester thus obtained, a solution of 10 g of benzoylvanillyl chloride in 250 ml of absolute benzene was added drop by drop. The reaction mixture was heated on the water bath for 3 hours, during the course of which sodium chloride gradually separated from the solution. The rest of the reaction was carried out similarly to the experiment described above. After the ether had been removed, the residue was twice distilled in vacuum. About 2 g of the ketone was obtained in the form of a yellowish viscous oil with b.p. 190-193° at 0.5 mm. Upon standing, the compound crystallized. After repeated crystallization from a mixture of ether and petroleum ether (1:1), 1.5 g of the compound was obtained with m.p. 39-40°, in the form of white platelets. It was soluble in the usual organic solvents, insoluble in petroleum ether and in water.

2.991 mg substance: 8.309 mg CO₂; 1.850 mg H₂O.
Found %: C 75.76; H 6.92.
C₁₈H₂₀O₃. Calculated %: C 76.04; H 7.04.

The 2,4-dinitrophenylhydrazones, after three recrystallizations from alcohol, was in the form of yellow needles with m.p. 136°.

4.510 mg substance: 0.480 ml N₂ (19°, 737 mm).
Found %: N 12.05.
C₂₄H₂₄O₆N₄. Calculated %: N 12.07.

4-Hydroxy-3-methoxyphenylethyl-γ-phenylpropyl ketone (III). To a solution of 8 g of γ-(β-phenylethyl)-acetoacetic ester in 70 ml of absolute alcohol there was added an alcoholic solution of sodium ethylate, prepared from 0.72 g of sodium in 80 ml of absolute alcohol. To the alcoholic solution of sodium phenylethyl-acetoacetic ester thus obtained, there was added a solution of 9.4 g of benzoylvanillyl chloride in 200 ml of absolute benzene, and the reaction solution was heated on the water bath for 3 hours. The reaction was carried out and the reaction product treated in the usual way to give about 2.5 g of 4-hydroxy-3-methoxyphenylethyl-γ-phenylpropyl ketone in the form of a faintly colored viscous liquid with b.p. 208-210° at 1 mm. The compound crystallized in the receiver. It was recrystallized from a mixture of ether and petroleum ether (2:8). M.p. 54-55°. It was in the form of colorless rectangular platelets, soluble in almost all organic solvents, insoluble in petroleum ether and in water.

3.310 mg substance: 9.296 mg CO₂; 2.175 mg H₂O.
Found %: C 76.59; H 7.35.
C₁₉H₂₂O₃. Calculated %: C 76.51; H 7.38.

The 2,4-dinitrophenylhydrazones, after recrystallization from alcohol, was in the form of yellow needles with m.p. 128-129°.

4.825 mg substance: 0.500 ml N₂ (19°, 739 mm).
Found %: N 11.77.
C₂₅H₂₆O₃N₄. Calculated %: N 11.73.

4-Hydroxy-3-methoxyphenylethyl-δ-phenylbutyl ketone (IV). To a solution of 4 g of γ-(γ-phenylpropyl)-acetoacetic ester in 40 ml of absolute alcohol there was added an alcoholic solution of sodium ethylate prepared from 0.36 g of metallic sodium in 40 ml of absolute alcohol. To the resulting solution there was added, drop by drop, a solution of 4.4 g of benzoylvanillyl chloride in 80 ml of absolute benzene. The reaction mixture was then heated on the water bath for 3 hours. After the reaction product had been treated in the usual way, about 1.5 g of 4-hydroxy-3-methoxyphenylethyl-δ-phenylbutyl ketone was obtained in the form of a yellowish viscous liquid with b.p. 212-214° at 2 mm.

2.966 mg substance: 8.366 mg CO₂; 2.032 mg H₂O.
Found %: C 76.93; H 7.67.
C₂₀H₂₄O₃. Calculated %: C 76.97; H 7.69.

The 2,4-dinitrophenylhydrazones of this ketone, after recrystallization from alcohol, was in the form of yellow needles with m.p. 138°.

3.980 mg substance: 0.422 ml N₂ (20°, 726 mm).
Found %: N 11.80.
C₂₆H₂₈O₆N₄. Calculated %: N 11.38.

SUMMARY

1. A number of ketones (HO)(CH₃O)C₆H₃CH₂CH₂CO(CH₂)_nC₆H₅ . (n = 1, 2, 3, and 4) has been synthesized by the condensation of benzoylvanillyl chloride with the

corresponding γ -substituted derivatives of acetoacetic ester, followed by saponification and decarboxylation.

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Received May 13, 1948.

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THE ALKALOIDS OF SALSOLA RICHTERI

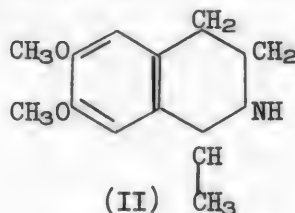
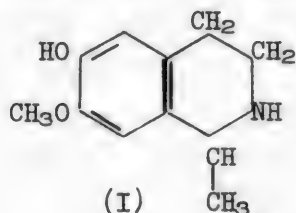
V. THE N-DERIVATIVES OF SALSOLIN AND SALSOLIDINE

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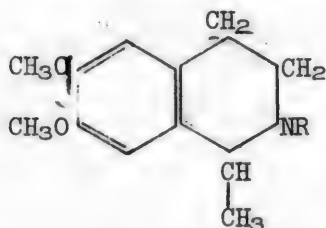
The alkaloids salsolin, $C_{11}H_{15}NO_2$, and salsolidine, $C_{12}H_{17}NO_2$, isolated in 1933/35 by A.P. Orekhov and N.F. Proskurnina [1,2] from the Central Asian plant Salsola Richteri (family Chenopodiaceae) are very valuable substances because of their ability to lower the blood pressure to a considerable degree [3]. Both salsolin and salsolidine in the form of their hydrochlorides have been accepted by the Medical Scientific Council as medicinal agents that produce high-quality hypertonia.

The structure of salsolin (I) and salsolidine (II), as has been shown by the same authors, can be expressed by the following formulas:



The object of the present work was to prepare a number of new derivatives of these two alkaloids. Of especial interest was the synthesis of compounds that would result in a more permanent lowering of the blood pressure than had been noted for salsolin and salsolidine.

The work was carried out so as to obtain derivatives substituted on the nitrogen. Thus, we synthesized salsolidine derivatives with the general formula:



- III. $R = CH_2CH_2N(C_2H_5)_2$; IV. $R = CH_2CH_2CH_2N(C_2H_5)_2$
V. $R = CH_2CH_2OH$; VI. $R = CH_2CH_2OCONHC_6H_5$;
VII. $R = CH_2CH_2OCOC_6H_5$; VIII. $R = CH_2CHOHCH_2OH$;
IX. $R = N=O$

Diethylaminoethylsalsolidine (III) and diethylaminopropylsalsolidine (IV) were obtained by condensing salsolidine with diethylaminoethyl chloride and diethylaminopropyl chloride by heating in a solution of toluene. They were in the form of liquids, and gave well crystallized hydroiodides and picrates.

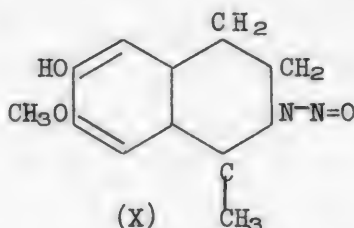
The condensation of salsolidine with ethylene oxide by heating in sealed tubes at 60° gave N- β -hydroxyethylsalsolidine (V) in the form of a liquid which formed a well crystallized hydrochloride. Upon heating with phenyl isocyanate, N- β -hydroxyethylsalsolidine gave a crystalline phenylurethane (VI). The benzoyl

derivative (VII) of N- β -hydroxyethylsalsolidine was obtained with some difficulty.

The condensation of salsolidine with glycidol, obtained by the method of T.H.Rider and A.J. Hill [4] gave salsolidine propanediol (VIII) in the form of a viscous oil. Of its salts, only the hydrochloride crystallized well. The condensation of salsolidine propanediol with phenyl isocyanate [5], instead of the expected phenylurethane, gave a polymerization product of phenyl isocyanate.

The nitrosation of salsolidine with amyl nitrite by heating in absolute alcohol led to the formation of nitrososalsolidine (IX) in good yield. When sodium nitrite was used for the same purpose, considerable tarring of the reaction mixture took place, and it was impossible to characterize the reaction products.

Nitrososalsolin (X) was also obtained only by the action of amyl nitrite upon salsolin, but its formation was accompanied by considerable tarring of the reaction mixture, which began almost from the first moment of heating. The yield of nitrososalsolin was very small (3-4%). Under milder conditions, no reaction took place.



Both nitroso derivatives were crystalline compounds, almost insoluble in water.

From a pharmacological investigation of the derivatives obtained, it appeared that none of these compounds could rival salsolin and salsolidine. The phenylurethane of N- β -hydroxyethylsalsolidine had local anaesthetic properties, but was somewhat toxic. The investigation of the nitroso derivatives was a difficult problem because of their insolubility in water.

EXPERIMENTAL

1. Diethylaminoethylsalsolidine (III). To a solution of 5 g of anhydrous salsolidine in 30 ml of absolutely dry toluene there was added 2.5 g of diethylaminoethyl chloride. There was a 30% excess of salsolidine. The solution was heated at 120-125°. There immediately began the separation of a voluminous crystalline precipitate. The heating was continued for 10 hours, until the formation of the precipitate, which was salsolidine hydrochloride, came to an end. The precipitate was filtered off with suction, and the toluene solution acidified with 10% HCl and extracted with water. The acid aqueous solution was neutralized, with the volume kept small, made alkaline with potash, and extracted with ether. After the ether had been distilled off, 2.65 g of a yellow oily precipitate was obtained. After distillation in vacuum, the substance remained liquid.

The Hydroiodide. Upon the addition of HI to the alcoholic solution of the base, a crystalline precipitate formed. After recrystallization from alcohol, it had m.p. 221-223°.

2.206 mg substance: 7.83 ml 0.1 N AgNO₃.

6.747 mg substance: 0.284 ml N₂ (20°, 743.5 mm).

Found %: N 4.72; I 45.08.

C₁₈H₃₀N₂O₂ · 2HI. Calculated %: N 4.98; I 45.19.

The Picrate. Upon the addition of alcoholic picric acid to an alcoholic solution of the base, the picrate precipitated. After recrystallization from acetone, it had m.p. 205-206°.

Salsolidine Hydroiodide (obtained for purpose of comparison). Upon the addition of HI to an alcoholic solution of salsolidine a precipitate formed. After recrystallization and drying at 105°, this melted at 121-122°. Undried, it melted at 105°.

2. Diethylaminopropylsalsolidine (IV). A solution of 6.5 g of anhydrous salsolidine and 3.6 g of diethylaminopropyl chloride in 30 ml of absolutely dry toluene were heated at 135°. The formation of a crystalline precipitate began very quickly. The heating was continued for 60 hours, until there was no more formation of the precipitate, which was salsolidine hydrochloride. The toluene solution was acidified with 10% HCl and extracted with water until all the product had been extracted. The acid solution was made alkaline and extracted with ether. After the ether had been driven off, 4.6 g of a yellow oil was left. Upon distillation in vacuum (4-5 mm), 3.55 g of a light yellow oil came over at a temperature of 190-196°. It did not solidify.

The Hydroiodide. Upon the addition of HI to an alcoholic solution of the base, the crystalline hydroiodide was obtained. After recrystallization from alcohol, it melted at 202°.

2.115 mg substance: 7.3 mg 0.1 N AgNO₃.

6.618 mg substance: 0.279 ml N₂ (19°, 732.5 mm).

Found %: N 4.67; I 43.83.

C₁₉H₃₂N₂O₂·2HI. Calculated %: N 4.86; I 44.09.

The Picrate. The mixing of aqueous solutions of the hydrochloride of the base and of picric acid gave a picrate. After recrystallization from alcohol, this melted at 195-196°.

3. N-β-Hydroxyethylsalsolidine (V). A solution of 8 g of anhydrous salsolidine in 10 ml of chloroform was heated in sealed tube together with 3.4 g of ethylene oxide, also dissolved in chloroform (the ethylene oxide was used in 100% excess of the theoretical amount). The heating was continued for 6 hours at 60°. After removal of the chloroform, the oily uncrystallized residue was converted by the addition of alcoholic HCl into the hydrochloride, which was purified by repeated boiling with acetone. The hydrochloride, recrystallized from alcohol, melted at 172-173°. It contained one molecule of water of crystallization, and without drying, melted at 109°. Yield 8 g, or 68% of theory.

4.607 mg substance: 2.347 mg AgCl.

5.563 mg substance: 2.860 mg AgCl.

5.370 mg substance: 0.253 ml N₂ (25°, 740 mm).

Found %: N 5.13; Cl 12.60, 12.70.

C₁₄H₂₁NO₃·HCl. Calculated %: N 4.87; Cl 12.35.

The free base, obtained from the hydrochloride, remained liquid.

4. The Phenylurethane of N-β-hydroxyethylsalsolidine (VI). 1 g of N-β-hydroxyethylsalsolidine was dissolved with heating in 10 ml of absolutely dry ether. To this solution there was added a solution of 0.47 g of phenyl isocyanate in several milliliters of absolute ether. The mixture was heated for five hours, until the odor of the phenyl isocyanate disappeared. The precipitate was filtered with suction and washed with ether, to give 1.21 g of a crystalline compound. After repeated crystallization from alcohol and drying at 105°, the phenylurethane melted at 149-151°. Yield 82.8% of theory.

3.847 mg substance: 0.263 ml N₂ (25°, 749 mm).

3.746 mg substance: 0.247 ml N₂ (21.5°, 753.5 mm).

Found %: N 7.55, 7.44.

C₂₁H₂₂N₂O₄. Calculated %: N 7.56.

5. Benzoyl-N-β-hydroxyethylsalsolidine (VII). To a solution of 1.05 g of

the base in 8 ml of toluene there was added 0.1 g of powdered soda and 0.7 g of benzoyl chloride. A slightly yellowish oil immediately began to separate out with the evolution of heat. The oil gradually acquired a greenish tint. After 3 hours of heating, the toluene solution was decanted off, and the thickened oil was treated with 10% HCl and extracted with ether. The ether solution was washed with a 5% solution of soda and dried over anhydrous sulfate. Removal of the ether by distillation left 0.9 g of the benzoyl derivative in the form of a colorless oil that did not crystallize.

After the hydrochloric acid solution had been extracted with ether, it was made alkaline with ammonia and again extracted with ether. After the ether had been removed by distillation, the residue gave a hydrochloride with m.p. 173°. A mixed test of this with the hydrochloride of N-β-hydroxyethylsalsolidine gave no m.p. depression.

6. Salsolidinepropanediol (VIII). 5 g of anhydrous salsolidine was placed in a flask, which was fitted with a stirrer, a condenser, and a dropping funnel. Into the latter was poured 2 g of glycidol, prepared according to the method of T.H. Rider and A.J. Hill [8]. The condenser and the dropping funnel were fitted with calcium chloride tubes. Upon heating on a boiling water bath, the salsolidine melted, and the glycidol was added to it drop by drop, with stirring. After the glycidol had been added, the heating was continued for some time more, all together for about an hour. The viscous, transparent reaction mixture was dissolved by heating in a small amount of alcohol, and to the solution there was added an alcoholic solution of HCl. The precipitate was filtered with suction and washed with acetone. 3.5 g of the hydrochloride was thus obtained. This was thoroughly purified by boiling with acetone. After repeated crystallization from alcohol, it melted at 196-198°.

0.218 g substance: 7.0 ml 0.1 N AgNO₃.

4.775 mg substance: 0.208 ml N₂ (27°, 751 mm).

Found %: N 4.75; Cl 11.39.

C₁₅H₂₃NO₄·HCl. Calculated %: N 4.41; Cl 11.18.

The base obtained from the hydrochloride remained liquid. It was difficultly soluble in ether, more soluble in benzene. It gave no crystalline salts other than the hydrochloride. It was difficult to benzoylate, and the benzoyl derivative remained in the form of an oil.

7. Nitrososalsolidine (IX). To a solution of 13 g of anhydrous salsolidine in 10 ml of absolute alcohol there was added 10 ml of freshly distilled amyl nitrite. The solution was heated on a water bath with a reflux condenser for 2.5 hours, the alcohol then evaporated off, and the crystallized mass washed several times with petroleum ether to remove traces of amyl nitrite. Recrystallization from 50% alcohol gave 5.6 g of a white substance with m.p. 86.5-87°. From the petroleum ether that had been used for washing, there crystallized out upon standing 2.9 g more of the substance with m.p. 86-87°. Yield 9.5 g, or 64.0% of theory.

2.255 mg substance: 0.233 ml N₂ (20°, 754.5 mm).

2.373 mg substance: 0.248 ml N₂ (20.5°, 754.5 mm).

Found %: N 11.75, 11.76.

C₁₂H₁₆N₂O₃. Calculated %: N 11.81.

Nitrososalsolidine was almost insoluble in cold water, more soluble in hot water. It dissolved well in alcohol.

8. Nitrososalsolin (X). To 3 g of salsolin there was added 50 ml of absolute alcohol and 5 ml of amyl nitrite. The mixture was gradually heated on a water bath with a reflux condenser. The salsolin, which was only slightly soluble in alcohol, slowly went into solution, being converted into nitrososalsolin. The

mixture quickly began to darken and very soon acquired an almost black color. The heating was discontinued, and the contents of the flask poured into a broad shallow vessel to permit the alcohol to evaporate in the air. The residue was in the form of a black tar. The tar was washed several times with petroleum ether. From this solution we were able to separate in all only 0.2 g of crystalline material. This was crystallized from 50% alcohol and had m.p. 130-131°. Yield 3-4% of theory. It was impossible to isolate individual substances from the tar.

2.481 mg substance: 0.277 ml N₂ (23°, 754.5 mm).

2.114 mg substance: 0.238 ml N₂ (21.5°, 748 mm).

Found %: N 12.53, 12.60.

C₁₁H₁₅N₂O₃. Calculated %: N 12.56.

Nitrososalsolin was almost insoluble in cold water and somewhat more soluble in hot. It dissolved well in alcohol.

SUMMARY

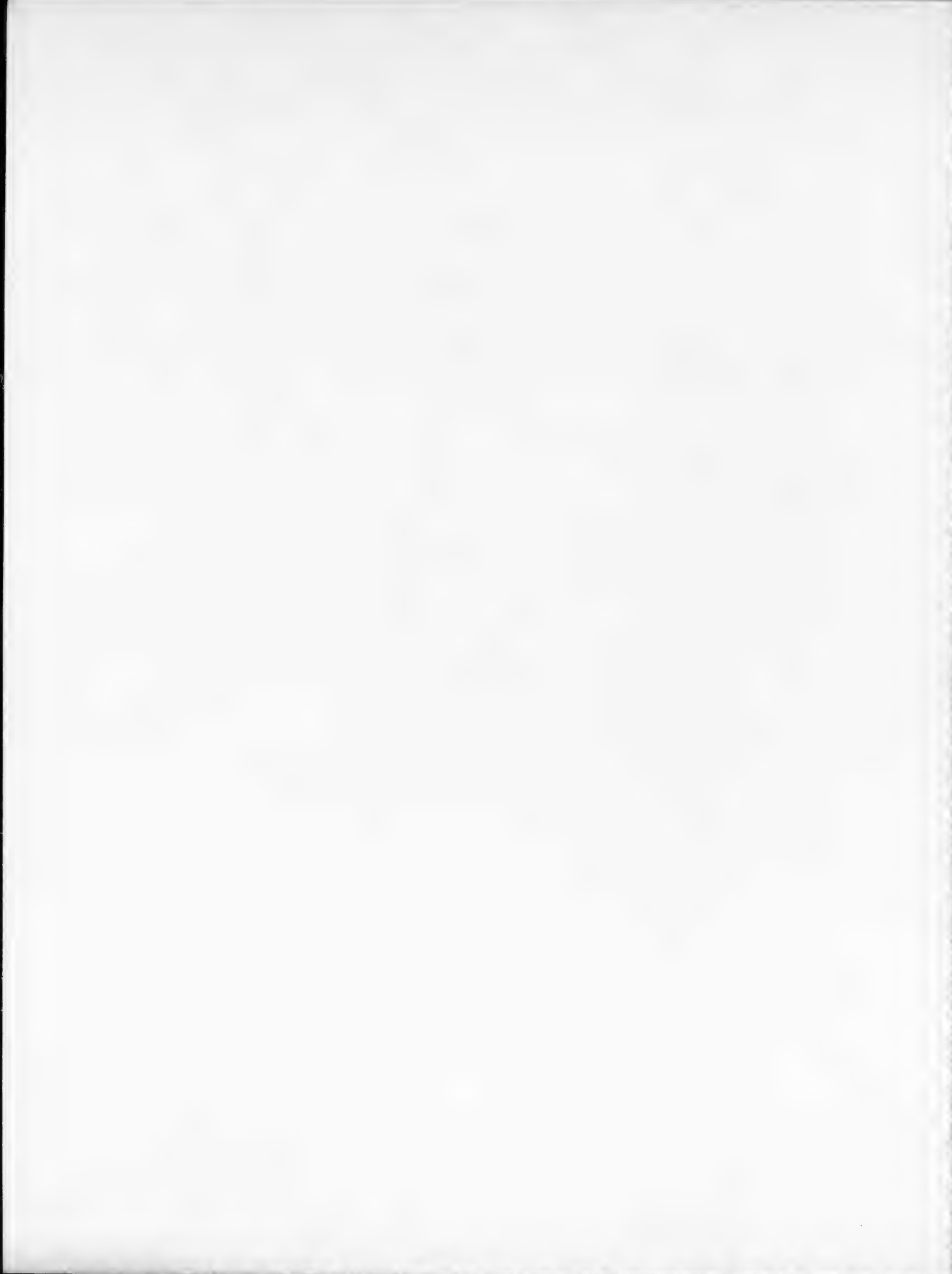
1. The following N-derivatives of salsolin and salsolidine have been synthesized: diethylaminoethylsalsolidine, diethylaminopropylsalsolidine, N-β-hydroxyethylsalsolidine, benzyl-N-β-hydroxyethylsalsolidine, the phenylurethane of N-β-hydroxyethylsalsolidine, salsolidinepropanediol, nitrososalsolidine, and nitrososalsolin.

2. In a pharmacological investigation of these derivatives, the phenylurethane of N-β-hydroxyethylsalsolidine appeared to be of more interest than the others. It had certain anaesthetic properties.

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A STUDY OF SULFONATION

XII. THE PREPARATION OF THE ACID CHLORIDE OF 1,5-NAPHTHALENEDISULFONIC ACID FROM ITS SODIUM SALT

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The acid chlorides of aromatic sulfonic acids are usually obtained either by the sulfonation with chlorosulfonic acid of compounds which do not have sulfonic acid groups, or by treatment of the sodium and potassium salts of the sulfonic acid with phosphorus chlorides. The action of phosphorus pentachloride is most often used as a method for the preparation of sulfonic acid chlorides from the sodium or potassium salts of sulfonic acids. We can also obtain sulfonic acid chlorides from the salts of sulfonic acids by the action of chlorosulfonic acid upon them. The latter method, however, is very seldom used, has not been well investigated, and is very briefly described in the chemical literature. None the less, the preparation of sulfonic acid chlorides from salts of sulfonic acids by means of chlorosulfonic acid is not without interest, as phosphorus pentachloride is not always accessible, and also because chlorosulfonic acid is a very inexpensive substance. In addition, in many cases the process of formation and isolation of the sulfonic acid chloride takes place more rapidly and more simply with chlorosulfonic acid than with phosphorus pentachloride.

The possibility of formation of a sulfonic acid chloride from sodium benzenesulfonate and chlorosulfonic acid was indicated in 1882 by Heumann and Köchlin [1].

V.M.Rodionov [2] described the conditions for the preparation of benzene and p-toluene sulfonic acid chlorides from the sodium sulfonates and chlorosulfonic acid with yields of about 65%. In other work, V.M.Rodionov and his coworkers [3] noted the possibility of the formation of the 1,5-naphthalenedisulfonic acid chloride from the 1,5-disulfonate of sodium and chlorosulfonic acid.

The formation of sulfonic acid chlorides by the action of chlorosulfonic acid on the potassium salts of benzenesulfonic acids substituted with chloro and nitro groups in the nucleus was later described briefly by Pollak and his coworkers [4]. Data on the formation of sulfonic acid chlorides by the action of chlorosulfonic acid on aminohydroxynaphthalenesulfonic acids with substituents in the amino group, on benzoylated and acetylated aminosulfonic acids, and on aromatic aminosulfonic acids with heterocyclic substituents can also be found in the patent literature [5].

The present work was primarily undertaken in order to investigate the method of preparation of sulfonic acid chlorides from the sodium salts of sulfonic acids by the action of chlorosulfonic acid. We determined how the extent of conversion of the sodium salt of 1,5-naphthalenedisulfonic acid into the chloride depended on the proportions of reagents, on the temperature, and on the duration of the reaction. In several experiments we also determined the influence of the moisture content of the sodium salt of the 1,5-acid, and of several mineral salts, on the yield and quality of the chloride.

The Influence of Temperature

In order to study the influence of the temperature on the yield and quality of the sulfonic acid chloride, the chlorosulfonic acid was mixed with the sodium salt of the 1,5 acid and the mixture maintained, with periodic stirring, for 2 hours at a predetermined temperature (Table 1). To 1 g of the salt, 2 ml of chlorosulfonic acid was added. This corresponded to 10 moles of the acid per 1 mole of salt, or 5 moles of acid per sulfonic acid group. After the mixture had been poured on ice, the chloride was filtered off, dried, and weighed. Its melting point was then determined.

TABLE 1

2 ml HSO_3Cl per 1 g of sulfonate. Mixture heated for 2 hours

Expt. No.	Temperature of Experiment	Yield of chloride (% of theory)	Melting point of chloride
5a	16°	6.0	179°
10	25	7.0	182
2a	40	49.0	179
33	65	86.0	182
58	85	85.1	182
52	85	85.8	182
17a	85	88.8	182
56	95	91.8	182
48	96	89.1	178 - 180
32	98	93.0	182
34	98	93.7	182
53a	100	85.4	182
42a	100	84.0	177 - 180
50	100	84.3	180
14	114	46.0	155-170

The results of the experiments, which are listed in Table 1, show that at room temperature the formation of the chloride takes place slowly. The velocity of the reaction increases rapidly with the temperature, and gives maximal yields of products from 95-98°, where the yields reach 93% of theory. Raising the temperature to 100° and higher not only does not increase the yield of chloride, but even lowers it, at the same time worsening the quality of the product. Thus, at 114°, the yield falls to 46%, and the melting point of the chloride to 155-170° (the m.p. of 1,5-naphthalenedisulfonyl chloride, according to the literature, is 183°). The cause of the worsened quality of the product is the beginning of a process of trisulfonation, and the formation of a trisulfonic acid chloride, whose admixture also lowers the melting point of the product.

This was shown by an experiment in which 2 g of the salt was heated with 4 ml of the chlorosulfonic acid at a temperature of 114° for 10 hours. The yield of sulfonic acid chloride amounted to 14% of the theoretical. The chloride obtained was hydrolyzed by heating with water in a sealed tube, and the chlorine in solution was determined by Volhard's method:

0.2112 g substance: 15.05 ml 0.1 N AgNO_3 .

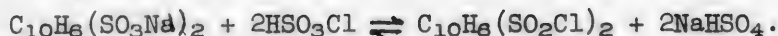
Found %: Cl 25.27.

$\text{C}_{10}\text{H}_5(\text{SO}_2\text{Cl})_3$. Calculated %: Cl 25.11.

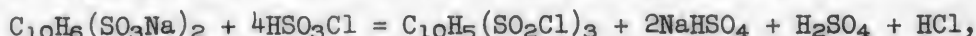
The melting point of the product obtained was 145°, i.e., it was almost pure 1,3,5-trisulfonic acid chloride (m.p. 146°).

The formation of the sulfonic acid chloride from the sulfonate takes place

according to the equation:



and is an equilibrium reaction. The formation of the trisulfonic acid chloride:



requires, instead of two, 4 molecules of chlorosulfonic acid, and results in the formation of sulfuric acid, influencing the course of the first reaction in the reverse direction to form the sulfonic acid or sulfonate. This is another reason for the decrease in yield of disulfonic acid chloride at a temperature of 100° or higher, when an admixture of the trisulfonic acid chloride is present.

Duration of the Reaction

The influence of the duration of the reaction between the reagents was studied at temperatures: 8-10°, 65°, and 100°. Here too, 2 ml of chlorosulfonic acid was added to 1 g of the sodium sulfonate. The results of the experiments are listed in the form of three series in Table 2.

TABLE 2
2 ml HSO_3Cl used per 1 g of sulfonate

Expt. No.	Temperature	Duration of the reaction (hours)	Yield of chloride (in % of theory)	Melting point of the chloride
1st series				
3	10°	6	5	179°
6a	10	24	28.0	182
55	10	192	88.9	182
26	10	552	91.3	181
27	10	864	89.7	179-181
30	10	2160	93.6	182
2nd series				
33	65°	2	86.0	182°
38	65	6	90.4	182
22	65	14	96.1	182
25b	65	25	96.0	182
3rd series				
1a	100°	0.5	70.6	179-180°
42a	100	2	84.0	177-180
44	100	4	79.8	176-178
47	100	6	74.9	175-178

The first two series indicate the equilibrium condition of the reaction. Thus, at 8-10°, the system reached a condition close to equilibrium after 200 to 500 hours, so that a further very lengthy period of reaction resulted in no significant shift of the reaction to the right.

In the second series of experiments, at a temperature of 65°, the equilibrium condition was approximately reached after only 14 hours of reaction.

The experiments carried out at 100° showed that the amount of chloride formed passed through a maximum. As the side reaction cited above took place, continuation of the reaction decreased the yield of chloride.

Proportions of Reagents

As the reaction of the sodium sulfonate with chlorosulfonic acid is an equilibrium reaction, the use of a considerable excess of chlorosulfonic acid can shift the reaction almost completely in the direction of chloride formation. The results of the pertinent experiments are listed in the form of two series in Table 3. These experiments, carried out at a temperature of 65°, show that the sodium salt of the 1,5-disulfonic acid can be converted into the chloride practically quantitatively, and that this reaction can be utilized in a number of cases for quantitative analysis and identification (expts. 23 and 43, Table 3).

TABLE 3
Temperature of Reaction 65°

Expt. No.	HSO ₃ Cl used (ml per 1 g of the salt)	Duration of the reaction (hours)	Yield of chloride (in % of theory)	Melting point of the chloride
1st series				
33	2	2	86.0	182°
19	3	2	88.2	182
18a	5	2	93.1	181
49	5	2	96.6	182
40a	5	2	96.8	181
2nd series				
20	2	6	88.7	182°
21	3	6	96.9	182
43	5	6	98.9	180
23	5	8	99.5	182
10a	10	6	100.7	175

Influence of the Moisture Content of the Sodium Sulfonate and of Admixtures of Mineral Salts

The moisture content of the sodium sulfonate showed a very great influence on the yield of chloride. The pertinent data are listed in Table 4, which gives the results of a number of experiments. To 1 g of salt there was added 2 ml of the acid, and the mixture was heated for 2 hours at 65 and 100°. The experiments showed that the salt containing 1.85% of moisture lowered the yield

TABLE 4
2 ml of HSO₃Cl used per 1 g of Sulfonate. Duration of Heating, 2 Hours

Expt. no.	Temperature	Yield of chloride (in % of theory)	M.p. of the chloride	Notes
1st series				
15	64°	73.4	181°	Moisture of salt 1.85% Salt dried at 120° Salt dried at 240°
17	64	80.6	181	
33	65	86.0	182	
2nd series				
12	100°	74.5	181	Moisture of salt 1.85% 1% water added to dry salt Salt dried at 240°.
40	100°	78.8	181	
42a	100	84.0	177-180	

in comparison with the dry salt by 10 to 12%. At the same time, drying of the sulfonate at 120° was insufficient. In order actually to dry the salt, it was necessary to keep it for 2 to 3 hours at a temperature of about 200°.

In the practical preparation of acid chlorides from sulfonates, it is very important to have data on the influence of admixtures of mineral salts in the sulfonate. The results of the experiments arranged to study this influence are listed in Table 5.

TABLE 5

Expt. No.	HSO ₃ Cl used (ml per 1 g of sulfonate)	Yield of chloride (in % of theory)	Melting point of chloride	Addition of min- eral salts to weight of sulfonate
11a	5	94.0	175-177°	No addition
12a	5	93.7	180	5% NaCl
19a	5	90.9	181	20% NaCl
13a	5	91.9	175-177	5% Na ₂ SO ₄
17a	2	88.8	182	No addition
15a	2	88.3	181	5% Na ₂ SO ₄

The reaction of the components was carried out at a temperature of 85° for two hours. The experiments show, however, that table salt and sodium sulfate had no appreciable influence on the yield and quality of the disulfonic acid chloride. The table salt and sodium sulfate were dried at 240-250°.

EXPERIMENTAL

The sodium salt of 1,5-naphthalenedisulfonic acid was prepared from the pure 1,5-disulfonic acid chloride with m.p. 183°. The latter was prepared according to the directions given by V.M. Rodionov [3]. The disulfonic acid chloride was subjected to hydrolysis in the presence of ethyl alcohol and water at a temperature of 80 to 100°. After complete solution of the chloride, the solution was evaporated to dryness on the water bath in order to remove the hydrogen chloride. The dry disulfonic acid was neutralized with caustic soda, crystallized, and dried at a temperature of about 200°.

Technical chlorosulfonic acid was subjected to distillation and used in the form of a transparent colorless liquid.

The experiments were carried out in the following manner. To a sample of 1 to 2 g of the sodium disulfonate, weighed out on an analytical balance in a wide-mouthed test tube, chlorosulfonic acid was added by means of a measuring pipette, and weighed. The mixture was stirred with a stirring rod that had a stopper on its upper end; this stopper, fitted with a bunsen seal, was closed, the stirring rod remaining in the test tube for the purpose of periodic stirring. Heating was carried out in an apparatus which was kept hot by steam, chloroform vapor, and alcohol-water vapor. In the experiments carried out at 10°, the mixture was kept in sealed tubes. After the reaction, the mixture was poured on ice, and the sulfonic acid chloride filtered off and dried. The melting point was then determined.

The sulfonic acid chloride did not hydrolyze at all at low temperatures, nor did it dissolve in water or in 5% sulfuric acid solution. The experiments on this point were carried out by treating a sample of the chloride at a temperature of 0° with continuous stirring with water or with 5% sulfuric acid for from 1 to 7 hours. In tests made with the filtered liquid, no hydrogen chloride was detected by the silver nitrate test. Even after boiling for 2.5 hours, samples did

not contain hydrogen chloride. This indicated the absence in the sample of soluble sulfonic acid chloride before boiling.

The sulfonic acid chloride was easily hydrolyzed only upon boiling with water or with 5% sulfuric acid. Thus, when 1 g of the chloride was boiled for 1 hour, the following amounts were hydrolyzed (Table 6; data from analysis of the filtered liquid).

TABLE 6

	Amount hydrolyzed (in g from 1 g).	
	Cl' by Volhard's method	by titration with 0.1 N NaOH
With 50 ml of water.....	0.454	0.457
With 50 ml of 5% sulfuric acid..	0.303	-

Thus, hydrolysis took place more slowly in 5% sulfuric acid than in pure water.

SUMMARY

1. The formation of 1,5-naphthalenedisulfonyl chloride from sodium 1,5-disulfonate and chlorosulfonic acid has been investigated to determine the influence of temperature, duration of reaction of reagents, and amount of the excess of chlorosulfonic acid.

2. Conditions are given for the easy formation of the sulfonic acid chloride in good yield and in high quality. At a temperature of about 100° and higher, the formation of a trisulfonic acid chloride becomes appreciable. With a great excess of the chlorosulfonic acid, the disulfonate can be quantitatively converted into the disulfonic acid chloride.

3. An admixture of mineral salts (NaCl , Na_2SO_4) has little influence on the yield and quality of the sulfonic acid chloride. Moisture in the sulfonate considerably lowers the yield of sulfonic acid chloride.

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